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THE UNIVERSITY OF ALBERTA

THERMODYNAMIC STUDY OF ALLOYS BY E.M.F. MEASUREMENTS:

THEORY AND APPLICATION TO LIQUID LANTHANUM-ZINC ALLOYS

by

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A THESIS

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The undersigned certify that they have read, and
recommend to the Faculty of Graduate Studies for
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MEASUREMENTS: THEORY AND APPLICATION TO

LIQUID LANTHANUM-ZINC ALLOYS"

submitted by JEAN-BAPTISTE P.F. LESOURD, in partial
fulfilment of the requirements for the degree of
Master of Science.

A B S T R A C T

The historical and theoretical backgrounds for thermodynamic studies of alloys by e.m.f. methods have been surveyed. The published theoretical thermodynamic studies on multicomponent systems, of particular interest in the case of multicomponent alloys investigated by e.m.f. methods, have been reviewed and some of the equations rederived.

The case of e.m.f. studies on binary zinc alloys has been reviewed.

The e.m.f. of cells of the type La(s)/LiCl-KCl (eutectic) - $LaCl_3$/(La - Zn, saturated liquid alloy) has been measured over the temperature range 450-600°C. Thermodynamic functions for the limiting lanthanum-zinc solid intermetallic compound existing in this range are: ΔG_f°, -58.8 kcal/mole; ΔS_f°, -53 cal/deg-mole; ΔH_f°, -97 kcal/mole at 450°C. The standard potential of the La(III)/La(0) couple was measured at 450°C as -2.883 V, mole fraction scale and Pt(II)/Pt(0) reference. The significance of these measurements for the electro-chemical separation of lanthanum and uranium is discussed.

A C K N O W L E D G E M E N T S

T A B L E   O F   C O N T E N T S

L I S T   O F   T A B L E S

L I S T O F F I G U R E S

LIST OF SYMBOLS

A: Coefficient in representation of regular solutions.

a,b: Integration limits.

a (with subscript): Activity (of subscripted component).

c: Number of components.

E: Electromotive force (e.m.f.).

F: Helmholtz free energy (U-TS).

F: Faraday constant.

f: Function of c-1 variables.

G: Gibbs free energy (H-TS, referred to as "free energy").

H: Enthalpy.

L: Limit.

n: Oxidation state or charge of ion.

n (with subscript): Number of moles (of subscripted component).

P: Pressure.

R: Gas constant.

S: Entropy.

T: Absolute temperature.

U: Energy.

V: Volume.

w.   Solubility (g/kg).

x (with subscript): Mole fraction (of subscripted component).

Z: Thermodynamic property (general).

z: (with or without subscript): Integral or partial molal value (for subscripted component) of Z. Small letters (with or without subscript) are also used for other extensive thermodynamic properties, such as G, H and S, to denote integral or partial molal values (for subscripted component) of these properties.

α: Lagrange multiplier.

γ (with subscript):   Activity coefficient (of subscripted component).

ΔG, ΔH, ΔS: Variations of G,H,S.

Δx_1,Δx_2: Difference between mole fractions in the liquid and the solid phase for components 1 and 2.

λ: Arbitrary number.

λ (with subscript):   Variable describing the composition of a multicomponent system (subscript may or may not refer to a particular component).

μ (with subscript):   Chemical potential (of subscripted component).

Subscripts

f: Refers to the variation of formation of a thermodynamic property for the compound following between brackets.

i,j,k, or specific integral number or chemical symbol:

Refers to a particular component.

o: Refers to a specific point (temperature, composition).

Superscripts

e: Refers to a change of excess.

m: Refers to a change of mixing.

o: Refers to a standard or reference state.

Other notations

e (between brackets):   Refers to a eutectic point.

l (between brackets):   Refers to the liquid state.

s (between brackets):   Refers to the solid state.

M (with or without subscript):   Chemical symbol.

B_1, B_2, C_1, C_2, I, P(l), P(s):   Points in figure 2, defined in text.

The meaning of other symbols used is the generally accepted meaning.

I. INTRODUCTION

This work is concerned with the study of thermo-dynamic properties of alloys by electrochemical methods, in general and in the particular case of liquid lanthanum-zinc alloys.

I-1. Historical survey

Within the earliest studies of alloys by e.m.f. methods were the investigation on amalgams by two German scientists, Von Türin [1] and Meyer [2], in 1890 and 1891. They expected to find the molecular masses of the metals dissolved in mercury from the e.m.f. between two amalgams of the same metal, at different concentrations. In 1898, Cady [3] showed that this was not a satisfactory method for the determination of molecular masses of solutes in mer-cury, and tried to explain deviations from ideality. Numerous e.m.f. studies on amalgams were made until 1920, in Germany [4-6] and in the United States, particularly by G. N. Lewis and his coworkers [7-10], who were able to calculate indirectly standard potentials for the alkali metals in water by using amalgam cells. Their work is still the best available on standard potentials of alkali metals. The cells used in such experiments were composed of two amalgams of different concentrations in a given metal as electrodes, and a solution of one of the ions

of this metal in water or an ionizing organic solvent
as electrolyte (since mercury is seldom less noble than
its solute, the electrolyte is a solution of one of the ions
of the solute rather than of mercury). In 1921, G. N.
Lewis [11] interpreted the results of Richards and
Daniels [12] concerning the e.m.f. of concentrated thallium
amalgam cells in terms of activities. Two years later,
in 1923, Gerke [13] reviewed the previous work on amalgams
and used the saturated amalgam data to calculate the free
energies of formation of intermetallic compounds of
mercury. At this date [14], investigators started using
molten salts as conductors, thus permitting the study of
alloys at higher temperatures. Both liquid alloys [15-18] and
solid alloys [19-21] have been the object of a large number
of e.m.f. experiments since then. This subject has been
reviewed [22-26]; e.m.f. studies of binary zinc alloys are
reviewed here. The concept of regular solution, intro-
duced in 1935 by Hildebrand [27], was found useful for the
interpretation of experimental results in intermetallic
solutions. Simultaneously, Seltz [28-30] applied e.m.f.
measurements in alloy systems to the determination of
binary diagrams. A further theoretical advance is due
to Darken [31] who, in 1950, obtained general thermodynamic
equations for ternary and multicomponent systems. The
theory of Darken has been modified and generalized [32-34].

It has been applied to ternary alloys [35-39].

Since 1950, other advances occurred in experimental methods; molten salt techniques were improved, particularly as far as purification is concerned [40-42]. Solid electrolytes, such as glasses [43], and non-ionic conductors [44,45] have been used.

I-2. E.m.f. measurements in binary alloys and directly related data.

The e.m.f. methods of study of a binary alloy between two metals involve e.m.f. measurements in cells such as:

Reference electrode/ionic conductor/M_1-M_2(alloy).

There are indeed many possibilities for the choice of the reference electrode and the conductor. One of the most convenient choices for the reference electrode is one of the pure components of the alloy, such as M_1, and for the conductor, an ionic conductor containing an ion of M_1, of charge n, M_1^{n+}. This choice is convenient because then the terms related to the ionic concentrations vanish, and the e.m.f. is characteristic of the alloy only. This discussion shall be restricted to this case, i.e. to cells of the form:

(-) M_1 (pure)/M_1^{n+}(in solution)/M_1-M_2(solution) (+).
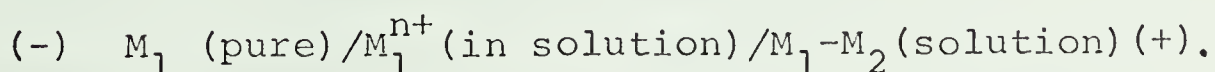
In order that this method yield reliable and easily interpretable data, the following conditions have to be fulfilled:

(a) M_1 is dissolved spontaneously in the M_1-M_2 solution, which means that the M_1 electrode is the anode (-) and that the M_1-M_2 solution is the cathode (+). In other terms, the free energy of formation of the M_1-M_2 solution has to be negative, otherwise no such solution can exist.

(b) The electrode processes which take place involve M_1 and M_1 only. M_1 must, therefore, be the more electropositive metal present, otherwise the M_1^{n+} cations would be reduced by the more electropositive metal M_2. Difficulties are likely to be encountered if M_1 and M_2 are not far enough from each other in the electrode potential series for the solvent being used. This point has been discussed quantitatively by Wagner and Werner [46].

(c) M_1 exhibits no other oxidation state than n under the experimental conditions.

In addition, various experimental problems have to be solved: the measured e.m.f.'s should be ascertained as the true equilibrium e.m.f.'s; there should be no

temperature gradient in the cell and no thermocouple e.m.f.'s in the electrodes; the electrolyte should be adequately purified and protected from contamination.

These conditions shall be assumed to be met in all the considerations which follow.

The electrode processes are:

At the anode   (-): M_1(pure) $\rightarrow$ M_1^{n+} + ne$^-$

At the cathode (+): M_1^{n+} + ne$^-$ $\rightarrow$ $M_1 - M_2$(solution).
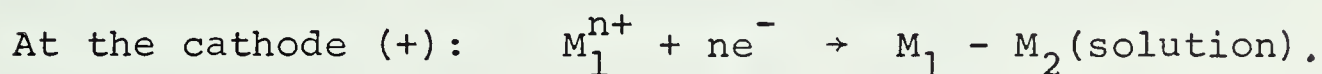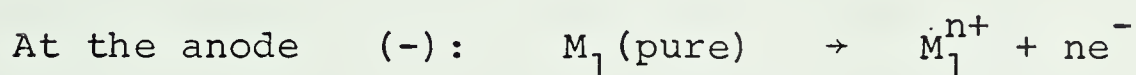
The spontaneous overall cell reaction is, therefore:

$$M_1(\text{pure}) \rightarrow M_1(\text{in solution}).$$
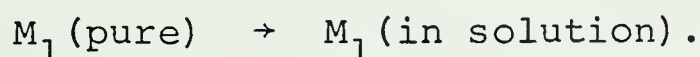
The free energy change for this reaction is: $\Delta G = \mu_1 - \mu_1^\circ$, where μ_1 is the chemical potential of M_1 in solution and μ_1° its chemical potential in the pure state under experimental conditions. If this is chosen as reference state, one has: $\mu_1 = \mu_1^\circ + RT \ln a_1$, where a_1 is the activity of M_1 in solution. Hence: $\Delta G = RT \ln a_1$. The cell e.m.f. E being, at constant pressure and temperature, related to ΔG by the equation: $E = -\Delta G/nF$, one obtains finally:

$$E = -(RT/nF)\ln a_1. \qquad (1)$$

Since $\mu_1 - \mu_1^\circ = g_1^m$, partial molal free energy of mixing of M_1 (1) can also be written as

$$g_1^m = nFE \qquad (2)$$

The partial molal entropy of mixing of M_1, s_1^m, is also

directly related to experimental data by:

$$s_1^m = nFdE/dT. \tag{3}$$

The partial molal enthalpy of mixing of M_1, h_1^m, is related to the e.m.f. by the Helmholtz equation:

$$h_1^m = nF(E-TdE/dT). \tag{4}$$

It is equivalent to calculate it from: $h_1^m = g_1^m + Ts_1^m$, or, as is done in the experimental part of this work, to obtain it by extrapolating g_1^m to 0°K.

I-3. Derivation of all thermodynamic properties of a binary alloy from e.m.f. measurements

First of all some basic thermodynamic concepts concerning solutions will be recalled. Consider a thermodynamic function Z which has extensive properties, such as V(volume), U(energy), H(enthalpy), S(entropy), F = U - TS, G = H - TS, where T is the absolute temperature. Any state of the system is a function of T, the pressure P and the number of moles of the c components n_1, $n_2 \ldots n_i \ldots n_c$, so that:

$$dZ = \left(\frac{\partial Z}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial Z}{\partial P}\right)_{T,n_i} dP$$
$$+ \sum_{i=1}^{c} \left(\frac{\partial Z}{\partial n_i}\right)_{T,P,n_j (j \neq i)} dn_i. \tag{5}$$

The partial molal property z_i for the ith component is,

by definition:

$$z_i = \left(\frac{\partial Z}{\partial n_i}\right)_{T,P,n_j}(j \neq i). \tag{6}$$

Unless otherwise specified, T and P will not be regarded as variables in what follows. To say that Z has extensive properties is to say that, whatever λ:

$$Z(\lambda n_1, \ldots, \lambda n_i, \ldots, \lambda n_c) = \lambda Z(n_1, \ldots, n_i, \ldots n_c).$$

Hence Z is a homogeneous function of degree 1, so that, from the Euler theorem and (6):

$$Z = \sum_{i=1}^{c} n_i z_i . \tag{7}$$

The integral molal property z of the system is defined as: $z = Z/\sum_{i=1}^{c} n_i = \sum_{i=1}^{c} x_i z_i$, where $x_i = n_i/\sum_{i=1}^{c} n_i$ is the mole fraction of the ith component. It is to be noticed that, from its definition, z_i is a homogeneous function of degree 0 of the n_i (or has intensive properties), whereby it is a function of c-1 independent variables having the dimensions of mole ratios. This will be important in the discussion of multicomponent systems.

The change of mixing of the property Z is defined as: $z^m = Z - \sum_{i=1}^{c} n_i z_i^{\circ}$, where the $^{\circ}$ superscript denotes a reference state, generally the pure state of the component under experimental conditions. It has

extensive properties, so that one can define integral
and partial properties of mixing. The same is true of
an excess property Z^e, defined as the difference between
the actual Z and the value that it would have in an
ideal solution, the latter being such that:
$\mu_i = \mu_i^o + RT \ln x_i$. The e.m.f. measurements discussed
here give g_1^m, s_1^m and h_1^m (equations (2), (3), (4)).
Equation (1) and (2) are equivalent, because:

$$g_i^m = RT \ln a_i \ . \qquad (8)$$

The latter equation defines the activity a_i of the ith
component in solution, with respect to a reference
state. The Gibbs-Duhem equation will give the partial
molal properties of M_2 from the partial molal properties
of M_1, which is enough for a complete knowledge of the
thermodynamic properties of the system. This equation,
obtained by differentiating (7) and comparing with (5)
and (6), at constant T and P, assumes the form:

$\sum_{i=1}^{c} x_i dz_i = 0$, or, for a binary system:

$$x_1 (dz_1/dx_1) + (1-x_1)(dz_2/dx_1) = 0 . \qquad (9)$$

The integration of (9) gives for one of the partial
molal properties of mixing obtained from e.m.f.
measurements:

$$z_2^m = - \int_0^{x_1} [x_1/(1-x_1)] dz_1^m \quad . \qquad (10)$$

Equation (10) can be modified if Z is the free energy, owing to (8), giving:

$$\log a_2 = - \int_0^{x_1} [x_1/(1-x_1)] d(\log a_1) , \qquad (11)$$

or, using the activity coefficients $\gamma_1 = a_1/x_1$ and $\gamma_2 = a_2/x_2$:

$$\log \gamma_2 = -\int_0^{x_1} [x_1/(1-x_1)] d(\log \gamma_1) \quad . \qquad (12)$$

Equations (11) and (12) are valid if M_2 in its pure state is chosen as reference for activities. The form (12) is the most convenient, since both $x_1/(1-x_1)$ and $\log \gamma_1$ remain finite except for $x_1 = 1$. It can be shown that for this limit, the integral is converging, since it can be rewritten as:

$$\log \gamma_2 = -[x_1 x_2 \log \gamma_1/(1-x_1)^2]_0^{x_1}$$
$$+ \int_0^{x_1} [\log \gamma_1/(1-x_1)^2 dx_1] \quad . \qquad (13)$$

The quantity $\log \gamma_1/(1-x_1)^2$ generally assumes a finite limit for $x_1=1$. This fact can be explained by the theory of regular solutions, due to Hildebrand[27]. In this theory, one obtains for $\log \gamma_1$ and $\log \gamma_2$ expressions of the form: $\log \gamma_1 = (A/2.3RT) x_2^2$ and

$\log \gamma_2 = (A/2.3RT)x_1^2$. Similarly, integrals in equations (10) to (13) can be shown to converge if the lower integration limit is taken as 1, but then one has to modify these equations in order to include $z_2^m(x_1=1)$ or $\gamma_2(x_2=1)$ unless the reference state for M_2 is chosen as the infinitely dilute solution of M_2 in M_1. Convergence requirements for the integration limit $x_1 = 1$ are found to be met for all extensive thermodynamic properties, in particular for H and S.

In conclusion, it appears that all the thermodynamic properties of the $M_1 - M_2$ alloy can, in theory, be calculated from the e.m.f. of the cell described previously. Since there is very little dependence of E upon P, these calculations are practically restricted to G, S and H.

As an example of such calculations, the work of Seltz [47] can be mentioned. This author applied various graphical methods of integration of the Gibbs-Duhem equation, using equations (11) to (13), to e.m.f. data for the zinc-antimony system.

I-4. E.m.f. measurements and binary phase equilibria

In alloy systems, binary liquid-solid phase diagrams can be obtained directly from e.m.f. measurements. More general thermodynamic methods can be applied to

the correlations of the data obtained from e.m.f. measure-
ments with the data obtained from binary phase equilibria.

I-4-1. Direct method of determination of phase diagrams

In a cell where the M_1 - M_2 alloy is liquid, the
e.m.f. can be studied at constant temperature and variable
composition. If the temperature is such that the liquidus
line is met, a break and a plateau are observed as sat-
uration is reached. Analysis of the liquid and the solid
phases beyond this break will give both the liquidus and
the solidus points at the temperature considered. In
many cases, however, it is not possible to separate the
liquid from the solid phase. The analysis of the whole
mixture at the break will then give the liquidus point.
For example, Hoshino and Plambeck [48] studied liquid
uranium-zinc alloys from the e.m.f. of the cell:

$$(-)U(s)/LiCl-KCl(eutectic) - UCl_3/U-Zn(Liq)^{(+)}.$$
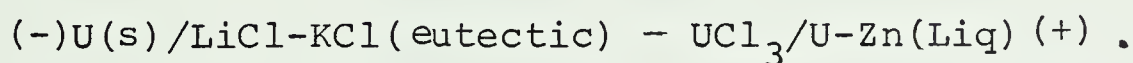
In this case, it is not possible to analyse separately
the liquid and the solid phases, but only to obtain
the uranium content of the alloy at the break (Fig. 1).
This was found by the authors [48] to be $x_U = 2.2 \times 10^{-2}$
mole p.c., at 808°K, falling between previous literature
values. Similar investigations were made by Volkovich
et al. [49], for the uranium-zinc system, and by Kober
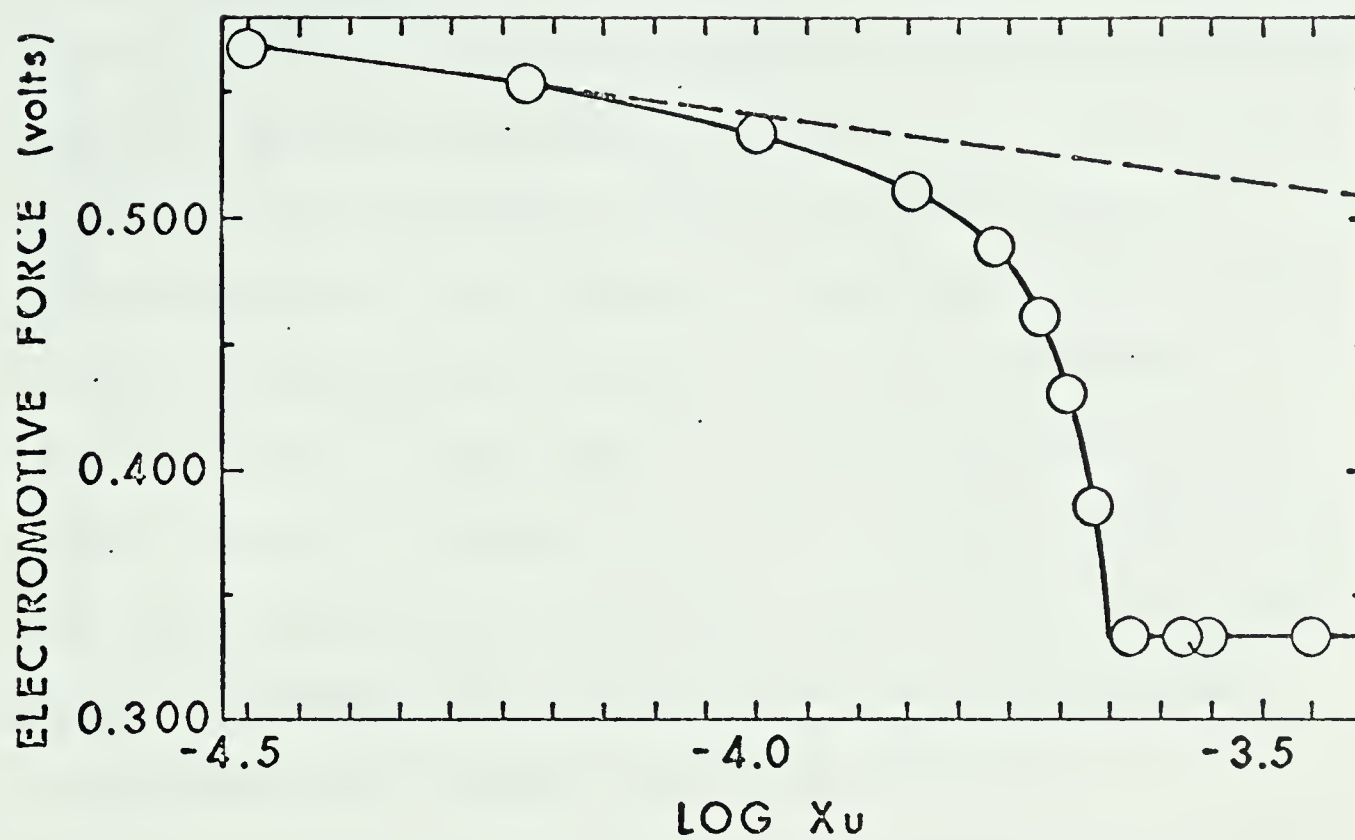
Figure 1. E.m.f. of the cell (-)U(s)/LiCl-KCl(eut.)-UCl$_3$)/U-Zn(+)(liq.) as a function of x_U, at 808°K (from the work of Hoshino and Plambeck [48]).

et al. [50], for the lanthanum-bismuth system.

If the liquidus line intercepts a constant-temp-
erature line at several points, the e.m.f.-composition
curve will show several plateaus. This has been
observed [51] in e.m.f. experiments on the uranium-bismuth
system, the phase diagram of which is not known; these
experiments established, however, the existence in
this diagram of four regions of constant uranium act-
ivity, corresponding to equilibria with compounds
including UBi_2, UBi_4, UBi.   In the same manner, the
e.m.f. study of Dubinin et al. [52], giving a small part
of the beryllium-zinc liquidus, which otherwise is not
known, provides some evidence that no intermetallic
compounds exist between beryllium and zinc.

I-4-2.   <u>Computational methods of determination of</u>

<u>phase diagrams</u>

I-4-2-1. <u>Complete miscibility in both the liquid</u>

<u>and the solid phases.</u>

If there is complete miscibility in both the liquid
and the solid phases, the phase diagram can be calcu-
lated according to the difference method proposed by
Seltz [28,29]. In this method, one plots at a constant
temperature T_O the activities of both components, M_1 and
M_2, with respect to a common standard state for each
component, in the liquid and the solid phase, against
the mole fraction of one of the components in the

corresponding phase (Fig. 2). If there is a liquid-solid equilibrium, one has: $a_1(l) = a_1(s)$, and $a_2(l) = a_2(s)$, where (l) and (s) refer to the liquid and the solid, respectively. In addition, the following equations can be written between the mole fractions: $x_1(l) + x_2(l) = 1$, and $x_1(s) + x_2(s) = 1$, whereby $x_1(l) - x_1(s) = x_2(l) - x_2(s)$, or, if: $\Delta x_1 = x_1(l) - x_1(s)$ and: $\Delta x_2 = x_2(l) - x_2(s)$, $\Delta x_1 = \Delta x_2$. The curves obtained by plotting Δx_1 and Δx_2 at constant activity of M_1 and M_2, respectively, will intercept at point I (Fig. 2), if the liquidus or the solidus lines are encountered at T_0. The abscissa of I gives one point of the liquidus (Fig. 2). The corresponding point of the solidus is obtained by taking the abscissa of point C_1 or C_2, where the activity is the same as in B_1 or B_2, which are the intercepts of a vertical line going through I, with the $a_1(l)$ and $a_2(l)$ curves, respectively (Fig. 2). From this construction, two points P(l) and P(s) of the diagram are obtained (Fig. 2). If the temperature is such that neither the liquidus nor the solidus lines will be encountered, the Δx_1 and Δx_2 curves will not intercept. They can also intercept at two points, if the phase diagram shows a minimum.
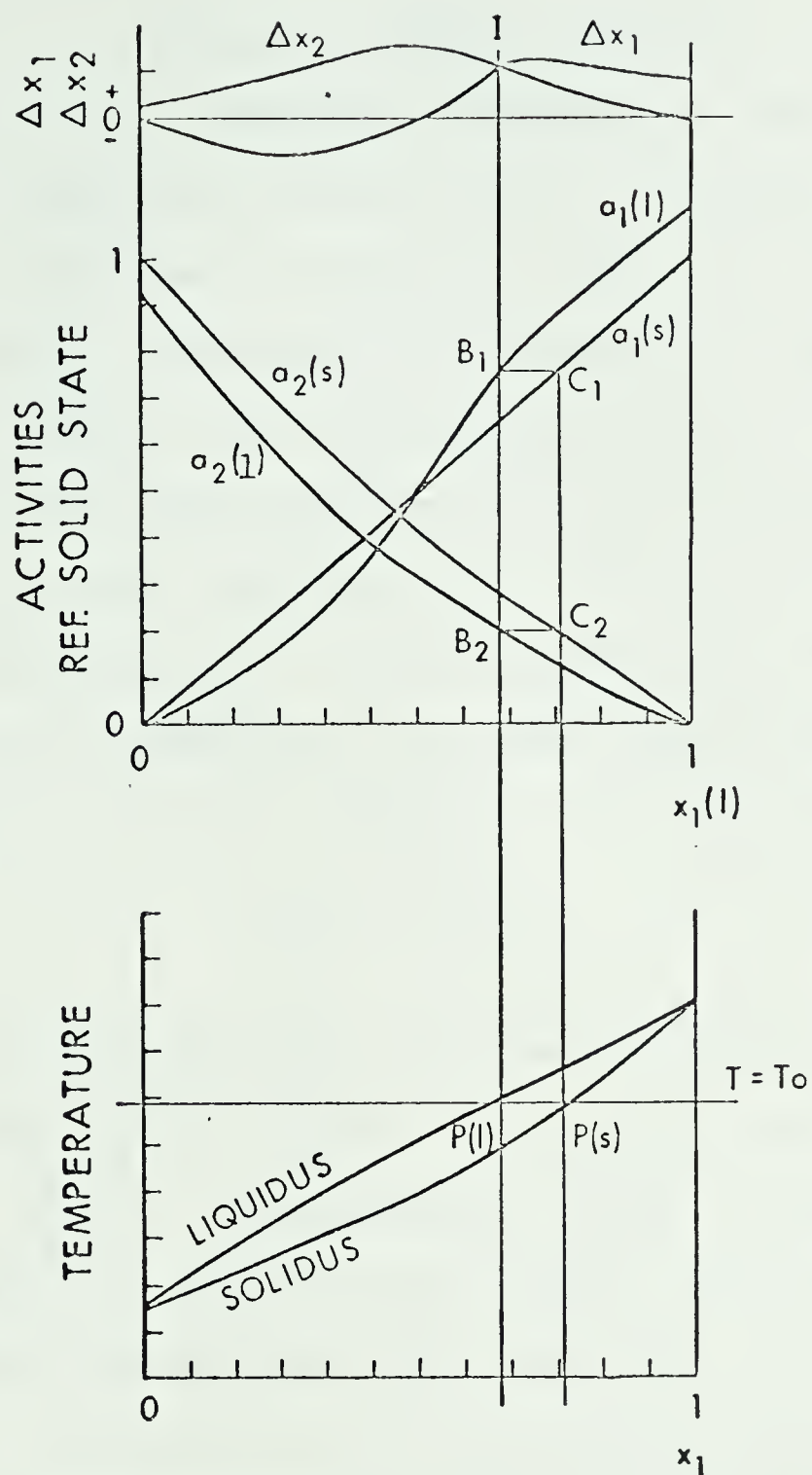
Figure 2. Application of the method of Seltz [28,29] to the computation of a phase diagram from activity data (complete miscibility in both the solid and the liquid phase).

I-4-2-2. Simple eutectic

If there is complete miscibility in the liquid phase, but no significant miscibility in the solid phase, a eutectic point may be observed (Fig. 3). The previous method is no longer applicable and can be replaced by another method, due to Dunkerley and Mills [23]. If $x_1(e)$ is the mole fraction of M_1 in the eutectic, for $x_1 > x_1(e)$, the liquid solution will be in equilibrium with pure solid M_1. On the liquidus line, the activity of M_1, with reference to the pure liquid state will be the same in both the liquid and the solid phases:

$$a_1(l) = a_1(s) .$$

$a_1(l)$ is obtained from e.m.f. measurements. $a_1(s)$ is such that: $\mu_1^o(s) = \mu_1^o(l) + RT \ln a_1(s)$, or: $RT \ln a_1(s) = \mu_1^o(s) - \mu_1^o(l)$. The quantity: $-(\mu_1^o(s) - \mu_1^o(l))$ is the free energy of fusion of M_1, easily obtained from standard thermodynamic data. The plot of: $(\mu_1^o(l) - \mu_1^o(s))/T$ vs. $1/T$ is a straight line (Fig. 3). Its intercepts with the plots of: $R \ln a_1(l)$ vs $1/T$ which are also straight lines, gives points of the liquidus. For example (Fig. 3), the $R \ln a_1$ vs. $1/T$ line for $x_1 = x_{10}$ intercepts the $(\mu_1^o(s) - \mu_1^o(l))/T$ vs. $1/T$ line for: $1/T = 1/T_O$; hence the point (x_{10}, T_O) of the liquidus. For $x_1 < x_1(e)$, the liquid is in equilibrium with M_2;

(MOLAL FREE ENERGIES)/T

$$\frac{\mu_1(l)-\mu_1^{\circ}(s)}{T}$$

$R \ln a_1(l)$

$x_1^{(II)} = x_{1\circ}$

$x_1^{(I)} = 1$

0

$$1/_T = 1/_{T_\circ}$$

$$1/_T \, (^{\circ}K)$$

TEMPERATURE

$T = T_\circ$

0

$x_1 = x_{1\circ}$

x_1

1
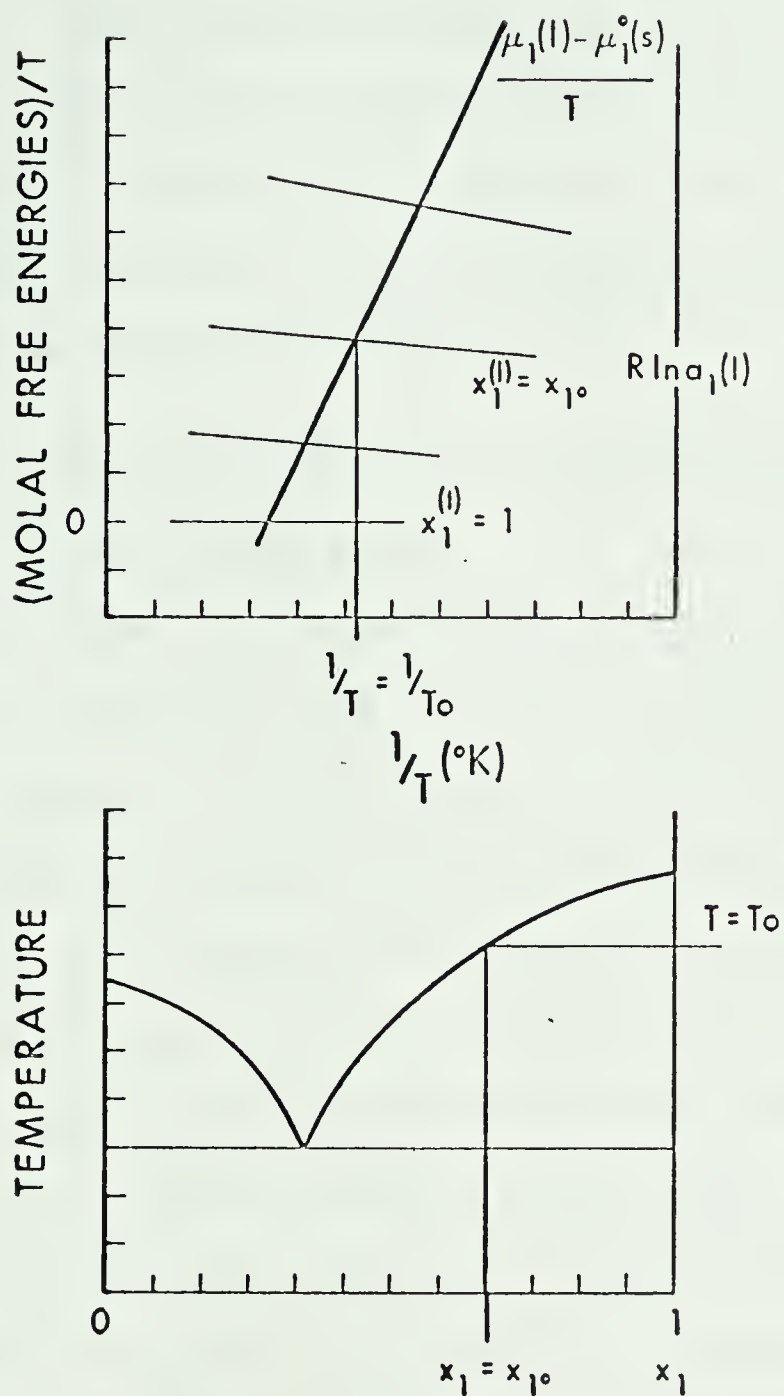
Figure 3. Application of the method of Dunkerley and Mills [23] to the computation of a phase diagram from activity data (simple eutectic).

a_2(l) is obtained by integration of the Gibbs-Duhem equation. This method was applied to the zinc-tin system, where no appreciable solid solubility exists [24], by Dunkerley and Mills [23]. The computed phase diagram is in good agreement with the diagrams previously obtained by thermal analysis [53-55].

I-4-2-3. Eutectic with partial miscibility
in the solid phase

Where there is a eutectic with a significant range of solid solubility (Fig. 4), e.m.f. measurements can also be applied. For example, the tin-bismuth phase diagram was studied by Seltz and Dunkerley [23,56]. In this work, the authors establish the β-solidus com-positions by writing, as in the previous case, that: a_{Sn}(l) = a_{Sn}(s), both activities being taken with respect to a common standard state, such as liquid tin. Assuming ideal behaviour of the β-solid solution, one obtains: x_{Sn}(s) = a_{Sn}(l)/a_{Sn}°(s), where a_{Sn}°(s) is the activity of pure solid tin. Accepting the published β-liquidus [57,58], a_{Sn}(l) being obtained from e.m.f. measurements and a_{Sn}°(s) from standard thermodynamic data, one can calculate from this relationship the β-solidus. The α-solidus was similarly calculated by the authors, and the α-liquidus was corrected to satisfy the above equation.
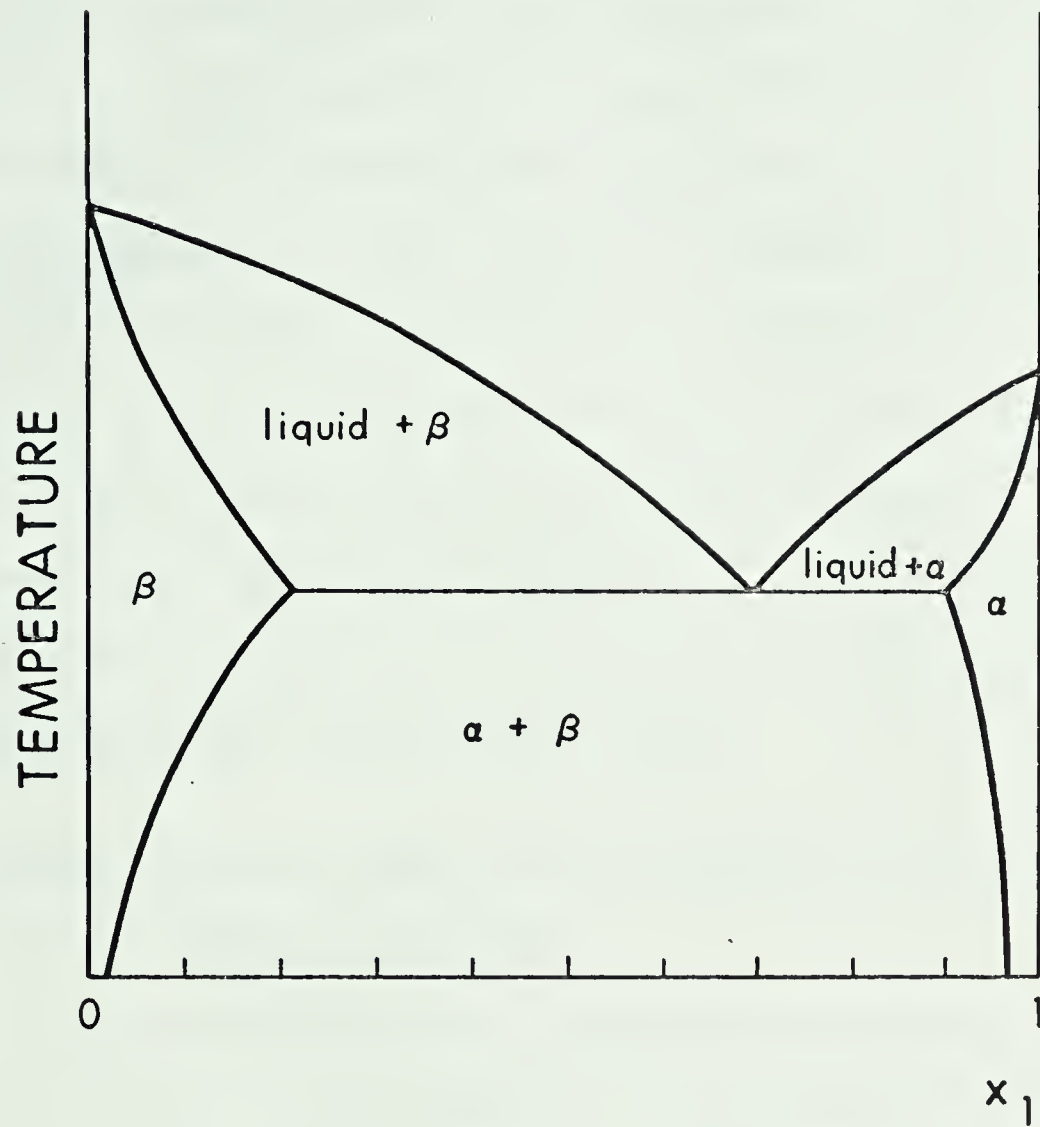
Figure 4. Phase diagram showing a eutectic with solid solubility.

I-4-2-4.   Other cases

Thermodynamic calculations from e.m.f. measurements also have ascertained the existence of a peritectic point in the lead-bismuth system [23,59,60]. Dunkerley and Mills [23] discussed the applications of e.m.f. measurements to other types of diagrams, such as diagrams including a monotectic, a eutectoid or a peritectoid. As an example of calculation of such a diagram, one can mention the e.m.f. works of Kleppa [61] and Rosenthal, Mills and Dunkerley [62], who calculated the monotectic point and the liquidus in the lead-zinc diagram which are reviewed below.

I-4-3.   Other types of correlation of e.m.f. data with phase equilibria

The calculation of a liquid-solid phase diagram from e.m.f. data is an example of direct correlation of the e.m.f. data with thermal analysis data concerning this phase diagram. Lumsden [63] gives more elaborate examples of such correlations, involving either the liquid-solid equilibria or the liquid-vapour equilibria (vapour pressure measurements).

White et al. [64] correlate e.m.f. data, vapour pressure data and calorimetric data in the silver-gold system.

I-5.   E.m.f. measurements and multicomponent alloys

I-5-1. General considerations

So far only binary alloys have been considered, but it is obvious that the e.m.f. methods of investigation can be extended to multicomponent alloys by using cells such as:

$(-) M_1 (pure) / M_1^{n+} (in\ solution) / M_1 ... M_i ... M_c (solution)\ (+)$,
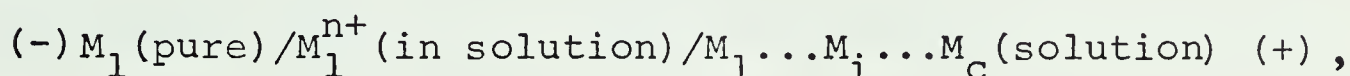
where c is the number of components. The conditions that have to be fulfilled by the system and with respect to experimental conditions are the same as for binary systems. Equations (1) to (4) are still valid, but the integration of the Gibbs-Duhem equation in binary systems is no longer valid. A more general theory will be derived here.

I-5-2. Calculation of an integral molal property from a partial molal property

Darken [31] found a method whereby values for an integral molal property of a system can be computed from values for one partial molal property. Balesdent [33] formulated the theory of Darken in a somewhat more general manner. This formulation will be used here.

Consider an integral molal property z and a corresponding partial molal property z_i. What is sought is a relationship between z and z_i. Let $z(x_1 ... x_i ... x_c)$ be

an analytical expression of z. This gives, by differentiating: $dz = \sum_{i=1}^{c} (\frac{\partial z}{\partial x_i}) dx_i$; the partial derivatives bear no subscripts because they are purely mathematical symbols: because of the relation: $\sum_{i=1}^{c} x_i = 1$, it is not possible, while x_i is varying, to keep all the other variables at an arbitrary constant value, so that the expression: $(\frac{\partial z}{\partial x_i})_{x_j (j \neq i)}$, where the subscript means that the derivation is made at constant x_j, for $j \neq i$, has no physical meaning whatsoever. Another expression of dz, obtained by differentiating: $z = \sum_{i=1}^{c} x_i z_i$ gives, taking into account the Gibbs-Duhem equation: $dz = \sum_{i=1}^{c} z_i dx_i$.

The constraint: $f(x_1 ... x_i ... x_c) = \sum_{i=1}^{c} x_i - 1 = 0$ being imposed on the system, the problem can be solved by a method similar to the method of Lagrange multipliers. α being the multiplier:

$$\sum_{i=1}^{c} (\frac{\partial z}{\partial x_i} - z_i - \alpha \frac{\partial f}{\partial x_i}) dx_i = 0. \qquad (14)$$

In order that the term in dx_1 vanish, one must have (taking into account $\frac{\partial f}{\partial x_i} = 1$): $\frac{\partial z}{\partial x_1} - z_1 - \alpha = 0$. If α is chosen to satisfy the latter equation, the c-1 remaining dx_i are now independent, so that (14) is identically zero, whereby: $\frac{\partial z}{\partial x_i} - z_i - \alpha = 0$, or:

$$z_i = \frac{\partial z}{\partial x_i} - \alpha, \qquad (15)$$

which is valid for all i's since it is valid for i=1.

Substituting z_i from (15) in: $z = \sum_{i=1}^{C} x_i z_i$, one gets:

$$\alpha = -z + \sum_{i=1}^{C} x_i \frac{\partial z}{\partial x_i}, \text{ so that (16) gives, for } i=1:$$

$$z_1 = z + (1-x_1)\frac{\partial z}{\partial x_1} - \sum_{i=2}^{C} x_i\frac{\partial z}{\partial x_i}. \qquad (16)$$

Equation (16) is applicable when an analytical expression of z is known. Let this be illustrated by two examples.

Example 1: A regular binary solution is defined by: $h^e = Ax_1x_2$, the entropy being the same as in ideal solutions, so that $s^e = 0$. Then: $g^e = Ax_1x_2$, whence, applying (16): $g_1^e = g^e + (dg^e/dx_1)(1-x_1) - x_2(dg^e/dx_2)$. This gives: $g_1^e = Ax_2^2$ and, similarly: $g_2^e = Ax_1^2$, or, in terms of activity coefficients: $\log \gamma_1 = (A/2.3RT)x_2^2$, and: $\log \gamma_2 = (A/2.3RT)x_1^2$. These expressions are identical to those mentioned above (I-3).

Example 2: In their work on the silver-gold system [64], White et al. obtain for the g^e of the liquid solution:

$$g^e = -(4656 - 800\, x_{Au} - 1.375T)x_{Au}(1-x_{Au}).$$

The application of (16) to this expression gives:

$$g_{Ag}^e = -(5456 - 1600\, x_{Au} - 1.375T)x_{Au}^2$$

and
$$g_{Au}^e = -(4656 - 1600\, x_{Au} - 1.375T)x_{Ag}^2.$$

These equations are identical to the equations obtained

by the authors by integration of the Gibbs-Duhem
equation, the form of which is identical to (16) in
binary systems.

Equation (16) can be modified to obtain an
expression more suitable for calculations from experi-
mental data. For this purpose, c-1 independent
variables $\lambda_1 \ldots \lambda_i \ldots \lambda_{c-1}$ must be chosen, whereby (16)
becomes:

$$z_1 = z - (1-x_1) \sum_{\substack{i=1 \\ (j \neq i)}}^{c} \left(\frac{\partial z}{\partial \lambda_i}\right)_{\lambda_j} \frac{\partial \lambda_i}{\partial x_1} - \sum_{\substack{i=1 \\ (j \neq i)}}^{c} \left(\frac{\partial z}{\partial \lambda_i}\right)_{\lambda_j} \sum_{k=2}^{c} x_k \frac{\partial \lambda_i}{\partial x_k} .$$

If the λ_i are so chosen that (taking into consideration:
$\sum_{i=1}^{c} x_i = 1$):

$$\sum_{i=1}^{c} x_k \frac{\partial \lambda_i}{\partial x_k} = 0 , \qquad (17)$$

for i ≥ 2, and $\lambda_1 = x_1$, equation (16) takes the form:

$$z_1 = z + (1-x_1)\left(\frac{\partial z}{\partial x_i}\right)_{\lambda_i} (i \geqslant 2) . \qquad (18)$$

Previous authors [31, 33] have chosen, in accordance with
(18): $\lambda_i = x_i/x_c$ for i ≥ 2. The one-dimensional part
of the phase diagram obtained by keeping the (x_i/x_c)'s
constant is called a pseudo-binary line, since (18) is
similar to the classical equation:

$$z_1 = z + (1-x_1)(dz/dx_1) \qquad (19)$$

obtained in binary systems from the Gibbs-Duhem equation.

In the triangular representation of a ternary diagram, pseudo-binary lines are straight lines passing through one corner (Fig. 5). It is to be noticed that equation (18) is not only valid for the set of variables which has just been introduced since it is valid for any set of λ_i's $(i \geqslant 2)$ that will satisfy (17), with $\sum_{i=1}^{c} x_i = 1$. It is easy to see that the acceptable forms of the λ_i's will be functions of the (x_i/x_c)'s, hence the importance of pseudo-binary systems in this theory.

In measurements such as e.m.f. measurements, z_1 is known and z unknown, so that one has to integrate (18). This gives:

$$z/(1-x_1) = [\lim_{x_1 \to a}[z/(1-x_1)] + \int_a^{x_1} [z_1/(1-x_1)^2]dx_1]._{\lambda_i(i \geqslant 2)}$$

(20)

The subscript λ_i indicates that the limit and the integral are calculated with the λ_i's $(i \geqslant 2)$ kept constant. This is of practical interest only if: $L = \lim_{x_1 \to a}[z/(1-x_1)]$ is obtainable. In general (as discussed by Vaisburd et al.[34]), the value $z(a)$ of z for $x=a$ must be known and L is finite. If $a=0$, this value is derived from the study of the $(c-1)$-component system $M_2...M_c$[31]. Therefore, for $a<1$:

$$z = (1-x_1)[z(a)/(1-a)] + \int_0^a [z_1/(1-x_1)^2 dx_1]._{\lambda_i(i \geqslant 2)}$$

(21)
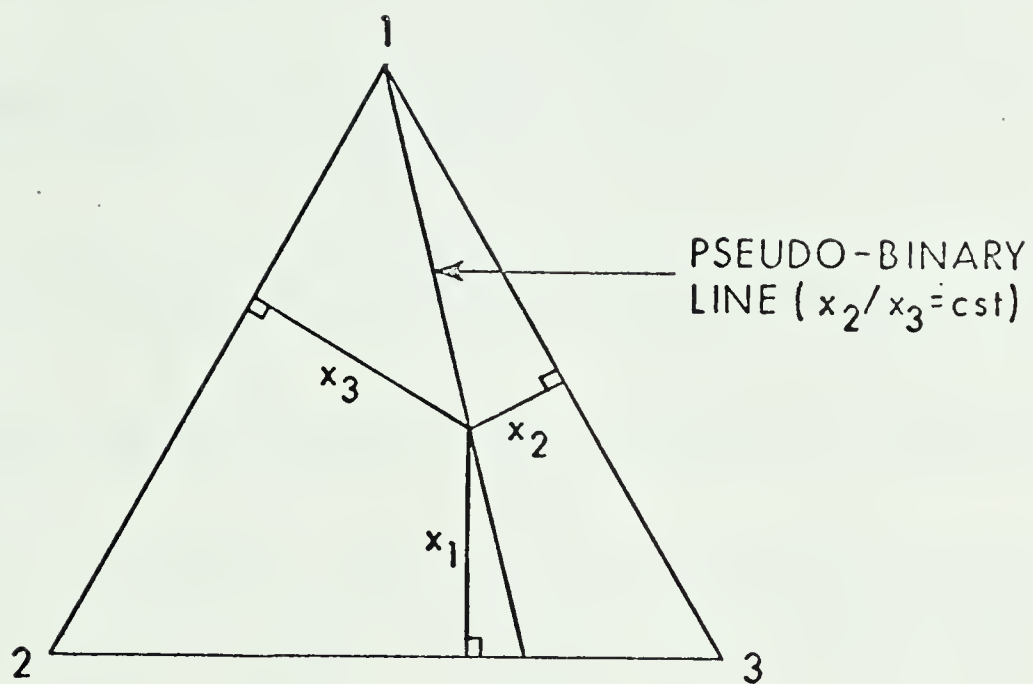
Figure 5. Representation of compositions in triangular coordinates for a ternary system, showing a pseudo-binary line.

For a=1, (21) is no longer valid but an equation can be derived if z is a property of excess z^e. According to the de l'Hopital theorem: $L = \lim_{x_1 \to 1} (\frac{\partial z^e}{\partial x_1})_{\lambda_i (i \geqslant 2)}$ whence,

applying (18): $L = -\lim_{x_1 \to 1} [(z_1^e - z^e)/(1-x_1)]$.

Since: $z^e = \sum_{i=1}^{c} x_i z_i^{\,e}$ and $x_i = (1-x_1)/(1 + \sum_{j \neq 1,i} x_j/x_i)$, one has

$L = \lim_{x_1 \to 1} [-z_1^e + \sum_{i=2}^{c} [z_1^e/(1 + \sum_{j \neq 1,i} x_j/x_i)]]$. The limit being

taken at constant λ_i's, i.e. at constant (x_i/x_c)'s, the terms $x_j/x_i = (x_j/x_c) \cdot (x_c/x_i)$ are constant and:

$L = (-z_1^e)_{x_1=1} + \sum_{i=2}^{c} [1/(1 + \sum_{j \neq 1,i} x_j/x_i)](z_i^e)_{x_1=1}$. If the

standard state is so chosen that for each component $z_i^e = 0$, (i.e. pure state for M_1 and infinitely dilute state in M_1 solution for the others) (20) becomes:

$$z^e = (1-x_1)[\int_1^{x_1} [z_1^e/(1-x_1)^2]dx_1]_{\lambda_i (i \geqslant 2)} \qquad . \quad (22)$$

If, however, the standard state is chosen as the pure state for all components, then (20) becomes:

$$z^e = (1-x_1)[\int_1^{x_1} [z_1^e/(1-x_1)^2]dx_1]_{\lambda_i (i \geqslant 2)} + \sum_{i=2}^{c} x_i (z_i^e)_{x_1=1} \quad .$$

$(z_i^e)_{x_1=1}$ can be calculated by integration of (19) on the

$M_1 - M_i$ binary line, which gives:

$$(z_i^e)_{x_1=0} = 0 = \lim_{x_1 \to 1} [\overset{e}{z}/(1-x_1)] + \int_1^o [z_1^e/(1-x_1)^2]dx_1].$$

On noting that: $z^e = x_1 z_1^e + (1-x_1)z_i^e$, this gives

$$(z_i^e)_{x_1=1} = -\lim_{x_1 \to 1} [z_1^e/(1-x_1)] - \int_1^o [z_1^e/(1-x_1)^2]dx_1.$$

Assuming that z_1^e is proportional to $(1-x_1)^2$ in the

vicinity of $x_1=1$, (regular behaviour for $z=g$) which is

generally true [31], one can see that the above limit is

zero, whereby:

$$z^e = (1-x_1)[\int_1^{x_1} [z_1^e/(1-x_1)^2]dx_1]_{\lambda_i (i \geqslant 2)}$$
$$+ \sum_{i=2}^{c} [\int_o^1 [z_1^e/(1-x_1)^2]dx_1]_{M_1-M_i \text{ binary}} \cdot \qquad (23)$$

The subscript "M_1-M_i binary" indicates that the inte-

gration is carried out on the M_1-M_i binary line.

Once z is known from z_1, or z^e from z_1^e, one can

obtain all the other partial molal properties by using

(18).

Elliott and Chipman [23,35,36, 65], Mellgren [66], and

other authors [37-39] have applied the method of Darken

to several ternary intermetallic systems studied by

e.m.f. methods.

I-5-3.   Calculation of a partial molal property

from another partial molal property

As has just been discussed, Darken [31] indirectly
solved this problem. Other authors [32,67-71] attempted to
solve it directly. This subject has been reviewed [72,73].

Since $dZ = \sum_{i=1}^{c} z_i dn_i$ is a complete differential,
one has:

$$\left(\frac{\partial z_2}{\partial n_1}\right)_{n_2} = \left(\frac{\partial z_1}{\partial n_2}\right)_{n_1} , \qquad (24)$$

the subscript n_1 indicating that the derivative is taken
at n_1 and all the other variables but n_2 constant, and
the subscript n_2 having a similar meaning. This is one
of the basic relationships between two partial molal
properties. From an experimental point of view, however,
the absolute numbers of moles are not practical variables.

Following the method used above, one can first use
the x_i as variables on a purely analytical basis. This
change of variables gives:

$$\frac{\partial z_2}{\partial x_1} - \sum_{i=1}^{c} x_i \frac{\partial z_2}{\partial x_i} = \frac{\partial z_1}{\partial x_2} - \sum_{i=1}^{c} x_i \frac{\partial z_1}{\partial x_i} . \quad (25)$$

Using $\lambda_1 \ldots \lambda_{c-1}$ as the c-1 independent variables for
practical calculations, one can see that, chosing
$\lambda_i (i \geqslant 3)$ as a homogeneous function of zeroth degree of
c-1 of the x_i's,   and independent of x_1 and x_2

(practically this will be restricted to $\lambda_i = x_i/x_c$ for
i ≥ 3), and λ_2 such that: $\dfrac{\partial \lambda_2}{\partial \dot{x}_1} = \overset{c}{\underset{i=1}{\sum}} x_i \dfrac{\partial \lambda_2}{\partial x_i}$, so that

the term in $\left(\dfrac{\partial z_2}{\partial \lambda_2}\right)_{\lambda_1}$ will vanish and integration will

be possible:

$$\left(\frac{\partial z_2}{\partial \lambda_1}\right)_{\lambda_2} \left[\frac{\partial \lambda_1}{\partial x_1} - \overset{c}{\underset{i=1}{\sum}} x_i \frac{\partial \lambda_1}{\partial x_i}\right] = \overset{2}{\underset{i=1}{\sum}} \left[\frac{\partial z_1}{\partial \lambda_i}\left(\frac{\partial \lambda_i}{\partial x_2} - \overset{c}{\underset{k=1}{\sum}} x_k \frac{\partial \lambda_i}{\partial x_k}\right)\right].$$

$$(26)$$

All the variables discussed below shall conform to the

above conditions, so that (26) will be applicable to

them. Gokcen [32] has chosen: $\lambda_1 = x_c/(1-x_2)$ and
$\lambda_2 = x_c/(1-x_1)$, which gives, from (26): $\left(\dfrac{\partial z_2}{\partial \lambda_1}\right)_{\lambda_2} \left(\dfrac{\partial \lambda_1}{\partial x_2}\right) =$

$\left(\dfrac{\partial z_1}{\partial \lambda_2}\right)_{\lambda_1} \left(\dfrac{\partial \lambda_2}{\partial x_1}\right)$ and integrating:

$$z_2(\lambda_1, \lambda_2) = z_2(0, \lambda_2) + \int_o^{\lambda_1} (\lambda_2/\lambda_1)^2 \left(\frac{\partial z_1}{\partial \lambda_2}\right)_{\lambda_1} d\lambda_1 \quad . \qquad (27)$$

The set of variables $\lambda_i = x_i/x_c$, for all i's gives similar

results.

In the theory of Wagner [67], generalized by Gokcen [32],

the variables were: $\lambda_1 = x_1$, $\lambda_2 = [1-(x_1+x_2)]/(1-x_1)$ and

$\lambda_i = (x_i/x_c)$ for $i \geqslant 3$. Then (26) gives:

$$\left(\frac{\partial z_2}{\partial x_1}\right)_{\lambda_2} = [\lambda_2/(1-x_1)^2]\left(\frac{\partial z_1}{\partial \lambda_2}\right)_{x_1} - [x_1/(1-x_1)]\left(\frac{\partial z_1}{\partial x_1}\right)_{\lambda_2}.$$

Upon integration, one obtains a general form of the equation of Wagner [67]:

$$z_2(x_1,\lambda_2) = z_2(a,\lambda_2) + \int_a^{x_1} [z_1/(1-x_1)^2]dx_1$$

$$- \int_a^{x_1} \lambda_2 \frac{\partial}{\partial \lambda_2}[z_1/(1-x_1)^2]_{x_1} dx_1 - [x_1/(1-x_1)]z_1(x_1,\lambda_2)\Big|_a^{x_1},$$

$$(28)$$

the integration being carried out at constant λ_2, x_i/x_c

($i \geqslant 3$). If the lower integration limit is chosen as

$a = 1$, one obtains, for a property of excess, by the

method already used for (22) and (23), the pure states

being taken as references for all components:

$$z_2^e(x_1,\lambda_2) = [\int_0^1 [z_1^e/(1-x_1)^2]dx_1]_{M_1-M_2 \atop \text{binary}} + \int_1^{x_1} [z_1^e(1-x_1)^2]dx_1$$

$$- \int_1^{x_1} \lambda_2 \frac{\partial}{\partial \lambda_2}[z_1^e/(1-x_1)^2]_{x_1} dx_1 - [x_1/(1-x_1)]z_1^e(x_1,\lambda_2),$$

$$(29)$$

the integration being carried out at constant λ_2, x_i/x_c

($i \geqslant 3$) except for the term bearing the subscript

"M_1-M_2 binary". The limit of $z_1/(1-x_1)^2$ is assumed

to be finite when $x_1 \to 1$.

Blander and Hagemark [71] used the same variables as Wagner [67]; the final formulae obtained by these authors for ternary systems are reported by Guion [73].

The set of variables $\lambda_1 = x_1$, $\lambda_i = x_i/x_c$ for $i \geqslant 2$, gives equations very similar to (28) and (29).

Another set of variables that has interesting properties consists of $\lambda_1 = z_1$, $\lambda_2 = x_2/x_c \ldots \lambda_{c-1} = x_{c-1}/x_c$. Since z_1 is generally not known analytically, but from experimental points, it is best to start from:

$(\frac{\partial z_2}{\partial \lambda_1})_{\lambda_2} = (\frac{\partial z_1}{\partial \lambda_2})_{\lambda_1}$, obtained with $\lambda_i = x_i/x_c$ for all i's,

and not from (27). This gives: $(\frac{\partial z_2}{\partial z_1})_{\lambda_2} (\frac{\partial z_1}{\partial \lambda_1})_{\lambda_2} = (\frac{\partial z_1}{\partial \lambda_2})_{\lambda_1}$, or:

$(\frac{\partial z_2}{\partial z_1})_{\lambda_2} = (\frac{\partial z_1}{\partial \lambda_2})_{\lambda_1} \Big/ (\frac{\partial z_i}{\partial \lambda_1})_{\lambda_2}$, and, regarding λ_1 as an

implicit function of λ_2:

$$(\frac{\partial z_2}{\partial z_1})_{\lambda_2} = - (\frac{\partial \lambda_1}{\partial \lambda_2})_{z_1} . \qquad (30)$$

McKay [68,69] and Schuhmann [70] carried out directly the integration of (30), which gives:

$$z_2(b, \lambda_2 \ldots \lambda_{c-1}) = z_2(a, \lambda_2 \ldots \lambda_{c-1}) - \int_a^b (\frac{\partial \lambda_1}{\partial \lambda_2})_{z_1} dz_1, (31)$$

where a and b represent two values of z_1. The function being integrated can be obtained, in ternary systems, by a geometric construction [70] using the constant z_1 curves

in triangular coordinates. The authors [68-70] actually started, not from (30) but from: $\left(\frac{\partial z_2}{\partial z_1}\right)_{n_2} = -\left(\frac{\partial n_1}{\partial n_2}\right)_{z_1}$, a straightforward consequence of (24). Gokcen [32] obtains from (30) not only (31) but also (28) and (29).

Experimental applications of this theory can be found in the articles quoted here [32,67-71,73]. Mostly ternary metal systems have been investigated, in many cases by e.m.f. methods. The work of Guion [73] is mentioned here, although the system investigated was not a metallic solution, but a ternary molten salt mixture: the experimental e.m.f. methods used are, in this work, very close to those used in metal systems.

I-5-4.   Conclusion on multicomponent systems

The theory of Darken [31], concerning the relationship between z and z_1, was derived according to a method due to Balesdent [33]. The basic assumptions of the theory are: (a) the extensive properties of Z and: (b) that Z is a well-behaved function of c variables at constant T and P. From these assumptions, equation (16) was derived, using the x_i as variables. This equation is of purely analytical interest, due to the constraint: $\sum_{i=1}^{c} x_i = 1$. Equation (18) was then derived with satisfactory independent variables, and integrated, leading to (21), (22), and (23). This method is extended here to the relationship between z_1 and z_2. From the same assumptions,

(25), an analytical equation, and (26), using adequate independent variables, were derived. Equations previously reported [32, 67-71] were found to derive from (25) or (26) by an appropriate choice of the independent variables. Some other choices have been proposed as examples.

This is a purely thermodynamic theory, in that it does not assume anything about the form of $z(x_1...x_c)$ or $z_1(x_1...x_c)$. This form is what is obtained in (for example) e.m.f. experiments.

Various authors, however, discussed models for metallic solutions [74-80]. The regular model, mentioned here for binary solutions, has been widely used. Except in a few cases [64], the results are satisfactory only in the low concentration range. Olson and Toop [75], having calculated the excess molal free energy in the Sb-Cd-Pb and Bi-Cd-Sn systems, from a regular model, compared their results with calculations from experimental e.m.f. data by the method of Darken [35,36,65,66]. The results showed that the model is only a first approximation, useful to estimate data where no literature is available.

I-6. Specific case of the lanthanum zinc system

In the experimental part of this work, liquid lanthanum-zinc alloys have been studied by e.m.f. methods. This investigation has been made in connection with

electrochemical processes for separation of fission impurities from uranium in liquid metal solutions.

In some methods of processing spent nuclear reactor fuels, the fuel is first dissolved in liquid zinc or liquid bismuth [81-84]. Numerous studies involving solutions of uranium in liquid metals have been made. Investigations concerning the separation of fission products by oxidation-reduction reactions have been conducted [85-87]. The diffusivity of uranium in liquid metal solutions has been measured [88]. Studies of dilute metallic solutions of uranium have been made by electromotive force methods, both in zinc [48,49,89] and in bismuth [90]. Solubility data for various metals in liquid zinc have been compiled by Johnson and Dillon [91].

It is well known that the fission of uranium-235 gives primarily one fragment of about 90 - 100 a.m.u. and another of about 135 - 145 a.m.u. In the first group, one finds nine isotopes of yttrium. In the second group, one finds seven isotopes of lanthanum, together with isotopes of cerium, praseodymium, neodymium and other rare earth metals [92,93]. Furthermore, stable isotopes such as Y-89, La-139, Ce-140 are the terminal products of decomposition of short-lived fission impurities [92,93]. It is therefore desirable to study

solutions of rare earth metals in liquid metals, as
they are typical fission impurities. The yttrium-zinc
system has been studied by Chiotti et al. [94] from
vapour pressure measurements; the e.m.f. study of
Hoshino and Plambeck [95] on this system has not yet been
published. E.m.f. experiments on the lanthanum-bismuth
system [50], on solutions of cerium and erbium in molten
zinc, lead, cadmium and bismuth [96] have been made. In
this work, the e.m.f. work done on binary zinc alloys has
been reviewed, and the lanthanum-zinc system, for which
no e.m.f. data appear to have been published, was experi-
mentally investigated. The phase diagram for this
system has been established by Vogel, Rolla, Iandelli
and Canneri [97]. Schramm [98] also studied this diagram,
but only in its zinc-rich part. Pascal [24] and Hansen
and Anderko [99] point out that there is disagreement on
the stoichiometry of the solid compound in equilibrium
with the solution in the zinc-rich part of the diagram.
According to Vogel et al. [97], this would be $LaZn_{13}$, whereas
Schramm [98] gives the formula $LaZn_{11}$. Veleckis et al. [100]
report the existence of both these compounds. For the
purpose of this thesis the formula $LaZn_{11}$ will be assumed;
the results are actually unchanged as long as the formula
includes one lanthanum atom. The aim of this investigation
was to study the saturated lanthanum-zinc solution in

the zinc-rich portion of the diagram, between 430°C

and 600°C, by measuring the electromotive force of

the cell: (-)La(s)/LiCl-KCl(eutectic)-LaCl$_3$/La-Zn(satur-

ated liquid alloy)(+). Experiments were also made to

establish the standard potential of the La(III)/La(0)

electrode in the fused LiCl-KCl eutectic at 450°C. This

potential has been determined only once [101] and in a

higher temperature range (480-550°C); the value calcu-

lated by Plambeck [102] at 450° is extrapolated from that

data.

I-7.   Review of e.m.f. studies of binary zinc alloys

These studies are discussed in some detail for

each group of the periodic chart and summarized in

Table 1. Indications on phase diagrams given, when

necessary, are taken from Pascal [24] and Hansen and

Anderko [99], and no attempt has been made to review the

data on the diagrams themselves, except when these

diagrams have been calculated from e.m.f. measurements.

I-7-1. Alloys of group I-A elements with zinc

None of these alloys appears to have been studied

by e.m.f. methods. Experimental difficulties are in-

volved with alkali metals: a solvent such as the eutectic

LiCl-KCl, for example, is decomposed by all these metals

except Li. Metallic solutions of alkali metals have,

however, been studied, using solid electrolytes (glasses)[43].

I-7-2.   Alloys of group I-B metals with zinc

The copper-zinc phase diagram shows a variety of solid intermetallic phases, which have been studied by Ölander [103] from the e.m.f. of the cells: Zn(1 or s)/LiCl-RbCl(eutectic)-$ZnCl_2$/Zn-Cu(s). This author investigated the entire region below the solidus, between 330 and 600°C and for x_{Zn} = 0.42 to 0.95. This involves the solid phases α, β, β', γ, δ, ε, η and some regions where two of these coexist.

The silver-zinc phase diagram is very similar to the copper-zinc diagram, with solid phases α, β, γ, ε, ζ, η. The e.m.f. of the cells: Zn(1)/LiCl-KCl(eutectic)-$ZnCl_2$/Ag-Zn(1 or s), has been studied, between 428 and 700°C, and for x_{Zn} = 0.28 to 0.84 [104,105]. This involves, below the solidus curves, the α, β, γ, and ε phases and regions where two of these coexist, and some regions above the solidus.

A partial e.m.f. work on the gold-zinc system has been made [106]. It involves the β' solid phase, between 380 and 550°C, for x_{Zn} = 0.44 to 0.55, and the cells under investigation are: Zn(1 or s)/LiCl-KCl(eutectic)-$ZnCl_2$/Au-Zn(s).

I-7-3. Alloys of group II-A metals with zinc

Practically nothing was known of the beryllium-zinc system before the work by Dubinin et al.[52], who studied the e.m.f. of the cell: Be(s)/LiCl-KCl(eutectic)-BeF$_2$/ Be-Zn(l), between 590 and 790°C and for $x_{Be} = 10^{-5}$ to 10^{-2}. A small part of the liquidus was thus established; the e.m.f. for saturated solutions being zero, the authors conclude that no intermetallic Be-Zn compounds exist.

E.m.f. studies of magnesium-zinc liquid alloys, involving the cells: Mg(s)/LiBr-KBr(eutectic)-MgBr$_2$/Mg-Zn(l) have been made [107], below the melting point of magnesium (650°C) and for $x_{Zn} = 0.03$ to 0.9. Thermo-dynamic data are extrapolated at 650°C. Eremenko and Lukashenko [108] use a different electrolyte in their cells, the LiCl-KCl eutectic, but their work on the Mg-Zn system, on a similar temperature and composition range, confirms the data of Terpilowski [107].

As in the case of alkali metals, no e.m.f. data seem to have been published for the alkaline earths-zinc alloys.

I-7-4. Alloys of zinc with other group II-B metals

Cadmium-zinc alloys have been studied by Taylor [14], between 430 and 570°C and for $x_{Zn} = 0.15$ to 0.85, from the e.m.f. of the cell: Zn(l)/LiCl-KCl(eutectic)-

$ZnCl_2$/Cd-Zn(l). Lumsden [63] contends that these measurements involve some error, owing to the closeness of the electrode potentials of Cd and Zn. Another e.m.f. study on these alloys has been made by Wynnemer [109] in a higher temperature range (700-900°C).

Zinc amalgams have been the object of many e.m.f. works [110-116]. These, however, cover only a small domain, between 18 and 30°C and for x_{Zn} going up to 0.06. In the work of Pearce and Eversole [115], the reference electrode was the most dilute amalgam, and the electrolyte was an aqueous solution of zinc sulphate. Clayton and Vosburgh [116], confirming the data of Cohen [111], report at 25°C a zero potential for the saturated amalgam against zinc.

I-7-5. Alloys of group III-B elements with zinc

No e.m.f. studies appear to have been made on the boron-zinc system. The aluminum-zinc system, which presents a eutectic with solid solubility, has been studied extensively by e.m.f. methods by Hilliard et al. [117]; the cells used were of the type: Al(s)/$AlCl_3$-NaCl(equimolecular)/Al-Zn(l or s), between 320 and 520°C and for x_{Zn} = 0.1 to 0.9. This covered the domains of stability of the α and α' phases, the α' + β domain, and some liquid solutions. The work of Eremenko [118] on this system involves cells of the type: Al(l)/NaCl-KCl(eutectic)-$AlCl_3$/

Al-Zn(l), between 670 and 850°C and for x_{Zn} = 0.14

to 0.95.

The e.m.f. of the cell: Zn(l)/LiCl-KCl(eutectic)-

ZnCl$_2$/Ga-Zn(l) has been measured [119] between 450 and

545°C and for x_{Zn} = 0.04 to 0.96.

The e.m.f. of the cells Zn(l or s)/LiCl-KCl(eut-

ectic)-ZnCl$_2$/In-Zn(l) have been measured [120] between

360 and 520°C and for x_{Zn} = 0.1 to 0.9.

Kleppa [61] reports unsatisfactory attempts to

study thallium-zinc alloys by e.m.f. methods, due to

the closeness of the electrode potentials of the two

metals.

I-7-6. Alloys of group IV-B elements with zinc

No e.m.f. studies appear to have been made on the

alloys of the first three elements of this column with

zinc.

The tin-zinc system has been studied by Taylor [14]

from the e.m.f. of the cell: Zn(l)/LiCl-KCl(eutectic)-

ZnCl$_2$/Sn-Zn(l), between 430 and 570°C, and for:

x_{Zn} = 0.1 to 0.9. The measurements of Fiorani and

Valenti [121], on the same cell, between 445 and 550°C,

and the e.m.f. results of Sano et al. [122] are in good

agreement with the study of Taylor [14]. The results of

this study were used by Dunkerley and Mills [23] to the

calculation of the tin-zinc phase diagram, which is of

the simple eutectic type, according to the above des-
cribed method. As has already been mentioned, there
was agreement with the previously published diagrams[53-55].
About the tin-zinc system, one can also mention the work
of Cleveland et al. [123], on the same cell, between 450
and 650°C, but for $x_{Zn} = 0.026$ to 0.12 only, in good
agreement with the above mentioned authors.

The lead-zinc system was studied by Kleppa [61],
from the e.m.f. of the cell: $Zn(1)/LiCl-KCl(eutectic)-$
$ZnCl_2/Pb-Zn(1)$, between 420 and 650°C and for $x_{Zn} = 0.04$
to 0.99. Rosenthal et al. [62] studied the same cell between
400 and 650°C and for the same composition range. Their
data are in very good agreement with the work of Kleppa[61].
Rosenthal et al. [62] used their e.m.f. data for the calcu-
lation of the Pb-Zn phase diagram, which presents a
miscibility gap in the liquid phase, by a method comparable
to the above described method for a diagram with a simple
eutectic. The monotectic existing on the zinc-rich side
and the eutectic existing on the lead-rich side were in
agreement with previous data [63, 123-126]. As for the
shape of the equilibrium curve between the two liquids,
it is not in agreement with some of the above authors[123, 126].

I-7-7.   Alloys of group V-B elements with zinc

No e.m.f. studies appear to have been made on the alloys of the first three elements of this column with zinc.

Seltz [47,127] measured the e.m.f. of the cell:

Zn(l or s)/LiCl-KCl(eutectic)-$ZnCl_2$/Sb-Zn(l) between 370 and 630°C, and for x_{Zn} = 0.1 to 0.9. The thermodynamic properties of the solid intermetallic compounds ZnSb, Zn_4Sb_3, Zn_3Sb_2 are calculated from these measurements.

The bismuth-zinc system was studied by Kleppa [61] from the e.m.f. of the cell: Zn(l)/LiCl-KCl(eutectic)-$ZnCl_2$/Bi-Zn(l), between 420 and 600°C and for x_{Zn} = 0.06 to 0.97; Lantratov and Tsarenko [128] also report e.m.f. data for this system, between 420 and 800°C and for x_{Zn} = 0.14 to 0.97. As in the lead-zinc case, these data give some information on the liquid miscibility gap in this system. The equilibrium curve between the two liquids, calculated by Kleppa [61], is not in agreement with the previous works of Haas and Jellinek [129] and Spring and Romanoff [130], but are in good agreement with some other authors [131-133].

I-7-8. Alloys of rare earth and transition metals

with zinc

Only the Y-Zn, La-Zn, Ce-Zn, Er-Zn and U-Zn systems have been studied by e.m.f. methods, in the respective

TABLE 1

Published e.m.f. studies on binary zinc alloys

Solute	Temp.(°C)	Types of cells	Ref.
Ag	430-700	Zn(l)/LiCl-KCl(eut.)-ZnCl$_2$/Ag-Zn(l or s)	104, 105
Al	320-520	Al(s)/AlCl$_3$-NaCl(equim.)/Al-Zn(l or s)	117
	670-850	Al(l)/NaCl-KCl(eut.)-AlCl$_3$/Al-Zn(l)	118
Au	380-550	Zn(l or s)/LiCl-KCl(eut.)-ZnCl/Au-Zn(s)	106
Be	590-790	Be(s)/LiCl-KCl(eut.)-BeF$_2$/Be-Zn(l)	52
Bi	420-600	Zn(l)/LiCl-KCl(eut.)-ZnCl$_2$/Bi-Zn(l)	61
	420-800	?	128
Cd	430-570	Zn(l)/LiCl-KCl(eut.)-ZnCl$_2$/Cd-Zn(l)	14
	700-900	?	109
Ce	400-550	Ce(s)/LiCl-KCl(eut.)-CeCl$_3$/Ce-Zn(l)	134
Cu	330-600	Zn(l or s)/LiCl-RbCl(eut.)-ZnCl$_2$/Zn-Cu(s)	103
Er	500-700	Er(s)/LiCl-KCl(eut.)-ErCl$_3$/Er-Zn(l)	134
Ga	450-545	Zn(l or s)/LiCl-KCl(eut.)-ZnCl$_2$/Ga-Zn(l)	119
Hg	18-30	Zn-Hg(l)$_1$/ZnSO$_4$ in H$_2$O/Zn-Hg(l)$_2$ or: Zn/ZnSO$_4$ in H$_2$O/Zn-Hg(l)	110-116
In	360-520	Zn(l or s)/LiCl-KCl(eut.)-ZnCl$_2$/In-Zn(l)	120
La	430-600	La(s)/LiCl-KCl(eut.)-LaCl$_3$/La-Zn(l)	This work, 134
Mg	420-650	Mg(s)/LiBr-KBr(eut.)-MgBr$_2$/Mg-Zn(l)	107
	420-650	Mg(s)/LiCl-KCl(eut.)-MgCl$_2$/Mg-Zn(l)	108
Pb	420-650	Zn(l)/LiCl-KCl(eut.)-ZnCl$_2$/Pb-Zn(l)	61,62
Sb	370-630	Zn(l or s)/LiCl-KCl(eut.)-ZnCl$_2$/Sb-Zn(l)	47,127
Sn	430-650	Zn(l)/LiCl-KCl(eut.)-ZnCl$_2$/Sn-Zn(l)	14,121-123
Tl		No stable e.m.f. in this system	61
U	420-850	U(s)/LiCl-KCl(eut.)-UCl$_3$/U-Zn(l)	48,49,89
Y	450-600	Y(s)/LiCl-KCl(eut.)-YCl$_3$/Y-Zn(l)	95

temperature ranges: 450-500, 430-600, 400-550, 500-700, and 400-850°C, in zinc-rich solutions up to saturation [95, this work, 134,96,48,49,89]. M being one of these metals, the cells used were of the type: M(s)/LiCl-KCl(eutectic)-MCl_3/M-Zn(l). The saturated solutions with Y, La, Ce and U are in equilibrium with intermetallic compounds which are probably: YZn_{11}, $LaZn_{11}$, $CeZn_{11}$ and U_2Zn_{17} [94,97,98, 100,135,136]. The work of Hoshino and Plambeck [95] on Y-Zn gives data roughly in agreement with those of Chiotti et al. [94]. The present work on La-Zn is in agreement with the unpublished data of Johnson [134]. The work by Hoshino and Plambeck on the U-Zn [48] system is in good agreement with e.m.f. studies [49,89] and other studies [136].

The e.m.f.'s for the saturated solutions of Y, La and Ce are, respectively, at 450°, for Y, La, and Ce 0.708, 0.850 and 0.762 volts, which seems to indicate that the properties of the intermetallic compounds in equilibrium with the liquid, probably YZn_{11}, $LaZn_{11}$ and $CeZn_{11}$, are quite similar.

II - E X P E R I M E N T A L

II-1   Apparatus (Fig. 6)

The glassware apparatus used was Pyrex and similar
to that used in previous electrode potential studies in
molten salts [137-139] and alloy studies by e.m.f. methods
involving molten salts [48-52,89-91,96]. The crucible
containing the molten salt was a flat-bottomed glass
tube.   It was contained in an envelope which consisted
of a round-bottomed glass cylinder on the wall of which
was blown a vacuum-cup stopcock (Corning 7544) connected
to a vacuum line.   This envelope was closed to the
atmosphere by means of a Pyrex cap connected to it with
a 75-mm O-ring joint.   On this cap were blown five 14/20
female ground-glass joints which were used to insert the
thermocouple well, gas inlet, gas outlet, and the elect-
rodes in the cell.   All these were such that the inside
of the envelope could be isolated from the outer atmos-
phere or maintained under vacuum when they had been
introduced.   This vacuum, of 10^{-2} to 10^{-4} torr, was main-
tained inside the envelope by a mercury diffusion pump
in series with a mechanical pump.

The thermocouple well consisted of 5-mm glass
tubing closed at its lower end, which was below the melt
surface, and connected at its upper end to a 14/20 male
ground glass joint.   The gas inlet consisted of 5 mm
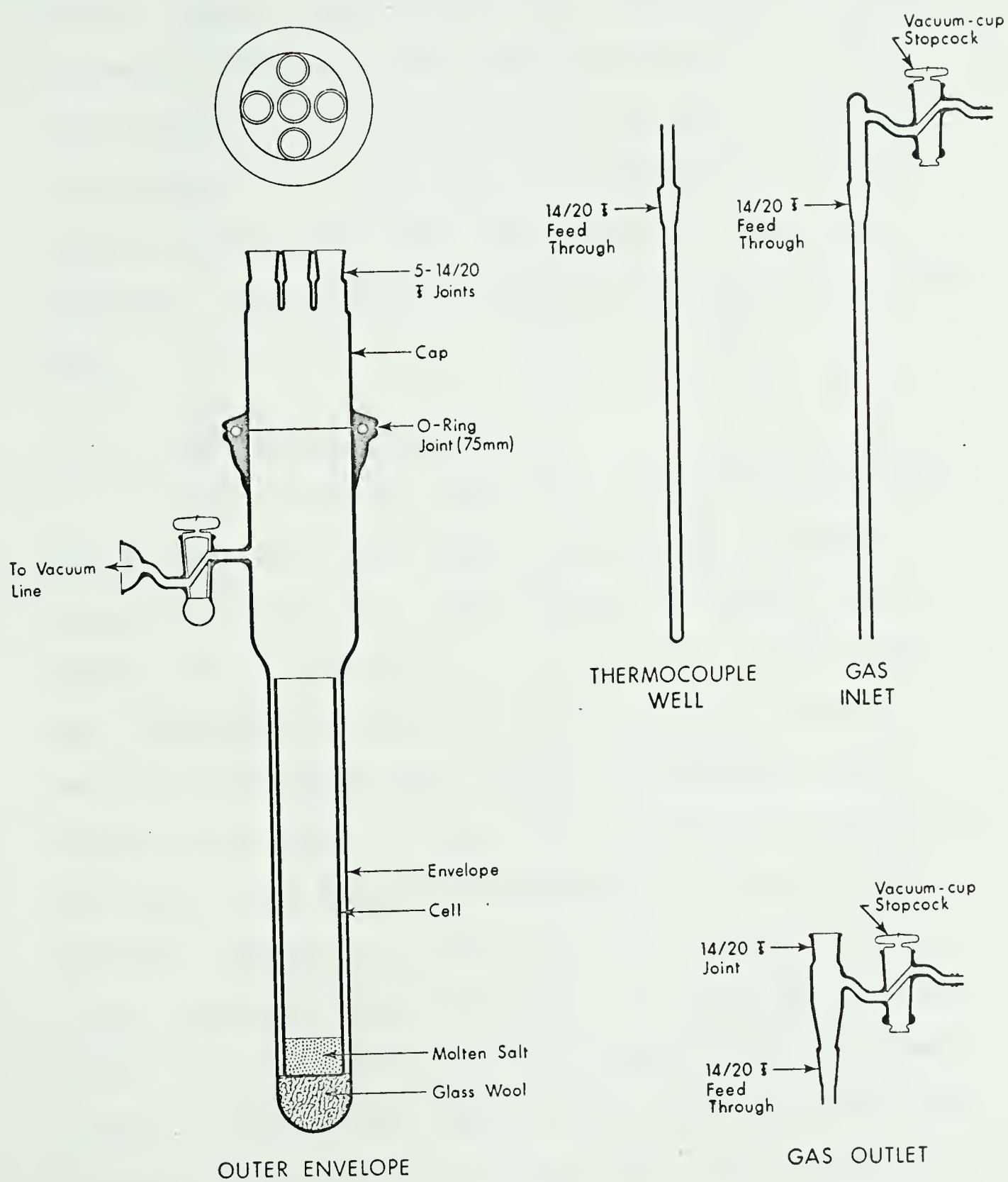
Figure 6. Glassware apparatus.

glass tubing connected to a 14/20 male ground-glass joint, sealed at its top, on the side of which was blown a vacuum-cup stopcock. Its lower end was above the melt. The gas outlet was a male 14/20 ground-glass joint on the side of which was blown a vacuum-cup stopcock; its upper end was connected to a 14/20 female ground-glass joint into which the inlet was inserted. The outlet was inserted in one of the 14/20 joints of the cap.

II-2. Electrodes (Fig. 7)

In the lanthanum electrode potential measurements, three electrodes were used: a lanthanum electrode, which was a 1/8" dia. and 5" length lanthanum rod (A.D. Mackay, Inc., New York, N.Y.) to which a copper lead was attached well above the melt level; a platinum reference electrode and a counter-electrode, each of which consisted of a large platinum flag (platinum wire and sheet from Engelhard Industries of Canada, Ltd., Toronto) welded to a copper lead and sealed to a 5-mm glass insulation tube below the lower end of the lead. These three electrodes were introduced in compartments made of a 12-mm glass tube closed with a fritted glass disc of porosity D or E (Ace Glass, Inc., Vineland, N.J.). The bulk of the melt acted as a salt bridge.

Kovar Seal →

Kovar Seal →

Kovar Seal →

10/30 ⚊ →
Feed
Through

10/30 ⚊ →
Feed
Through

10/30 ⚊ →
Feed
Through

Copper →
Lead

Copper →
Lead

Copper →
Lead

Weld →

Tungsten →
Wire

La Rod →

Weld →

Seal →
Pt. Flag →

Uranyl →
Glass
Zn Pool →
Tantalum →
Crucible

LANTHANUM
ELECTRODE

PLATINUM AND
COUNTER
ELECTRODES

ZINC POOL
ELECTRODE
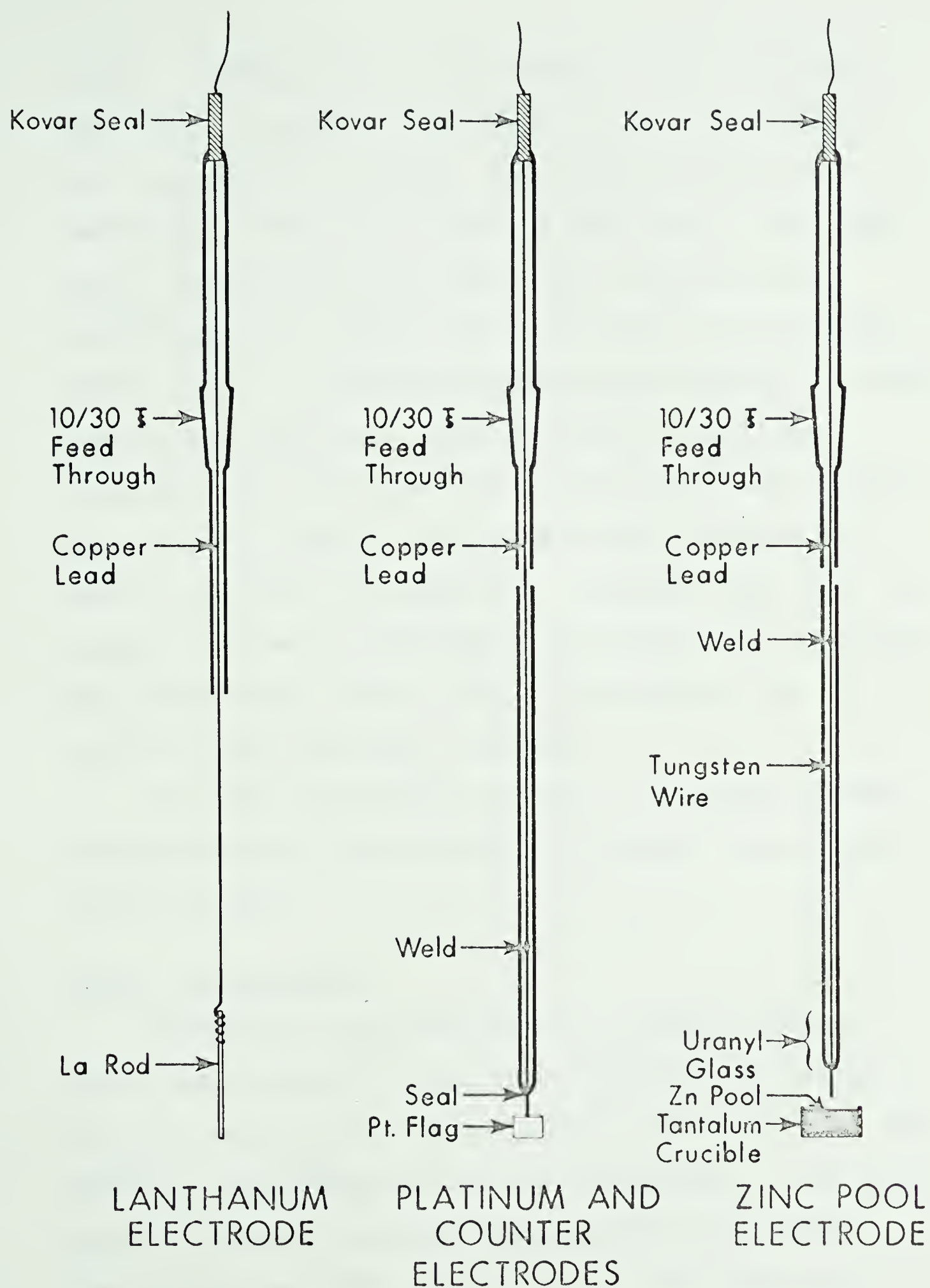
Figure 7.   Electrodes.

In the lanthanum-zinc alloy studies, two electrodes were used: a lanthanum electrode, as described above, and a zinc pool electrode. The liquid zinc was contained in a tantalum crucible on the bottom of the cell tube. Contact to it was made with a tungsten wire (0.020" dia; A.D. Mackay, Inc., New York, N.Y.) dipped in the liquid zinc at its lower end and welded to a copper lead at its upper end; this wire and the lead were insulated with 5-mm glass tubing, the lower end of which, made of uranyl glass, was sealed to the tungsten wire about 1 cm above its lower end. At their upper end, the copper leads were sealed through a Kovar seal to a 10/30 male feedthrough which could be inserted in one of the joints of the cap using a reducer.

To avoid thermocouple effects, connections between different metals were all made in the hot central region of the furnace.

II-3.   Instruments

Potentials were measured with a Hewlett-Packard Model 3400A digital voltmeter. A Model IV coulometric current source (E.H. Sargent and Co., Chicago, Ill.) was used for electrodepositions and anodizations. The bottom part of the cell envelope was inserted in a Lindberg Hevi-Duty Type 54381A furnace with a Type 59344 temperature control unit. A constant temperature could be

maintained in the cell within 1°C. Temperatures were measured with a chromel-alumel thermocouple calibrated at the zinc melting point. The thermocouple e.m.f. was measured with the digital voltmeter.

II-4.   Preparation of molten salt

A modification of the   method of Maricle and Hume[42] was used. The anhydrous, crystalline, reagent grade lithium and potassium chlorides (The McArthur Chemical Co., Ltd., Montreal) were mixed thoroughly in eutectic proportions. About one mole percent anhydrous lanthanum trichloride (A.D. Mackay, Inc., New York, N.Y.) was added in the case of the lanthanum-zinc alloy experiments. The mixture was progressively heated under vacuum (10^{-3} to 10^{-4} torr) to 450°C and maintained under these conditions for twelve hours in the crucible and envelope previously described. Then argon was introduced in this envelope and the crucible transferred to a Hevi-Duty Model 80 furnace under the fume hood where chlorine was bubbled through the melt for one hour.   Argon was bubbled through for four to six hours to remove the chlorine. The melt was then poured into glass tubes that were sealed under argon for storage of the frozen melt.

II-5.   Preparation of lanthanum-zinc alloys

About twenty grams of reagent grade zinc shot (May

and Baker Ltd., Dagenham, Essex, England) were melted in a small glass tube under zinc chloride. The zinc piece obtained was carefully washed, dried and polished in order to eliminate surface zinc oxide and chloride. It was then cut into smaller pieces and introduced in a 1" O.D. x 7/16" deep tantalum crucible (A.D. Mackay, Inc., New York, N.Y.) together with several previously polished small pieces of lanthanum weighing from 0.3 g to 1.0 g. The crucible was then set on the bottom of the glass envelope described above, under a flow of argon at 500°C, for fifteen to twenty hours. The piece of alloy was easily removed from the crucible after cooling down, owing to its contraction, then carefully polished and stored until use.

II-6.   Procedure

A tube of purified melt was opened. The salt was introduced in the cell under argon and maintained under vacuum (10^{-3} to 10^{-4} torr) at 400°C for twelve hours. Then argon was introduced while the electrode system was set up. This argon was purified by successive passage over hot copper, magnesium perchlorate, titanium sponge at 900°C (the use of a titanium sponge as a nitrogen adsorbent has been described previously [140]) and magnesium perchlorate. The cell was put under vacuum again. In the La(III)/La(0) electrode potential measurements, the

platinum reference electrode was first anodized until a mole fraction of 5 x 10^{-4} to 10^{-3} in Pt(II) was reached in the corresponding compartment. Similarly, mole fractions of La(III) from 10^{-4} to 3 x 10^{-3} were obtained in successive generations in the lanthanum compartment. After each generation, the lanthanum electrode was rotated in order to obtain a homogeneous concentration of La(III) in the compartment rapidly. Its potential against the platinum reference and the temperature were then taken as a function of time. The mole fractions of ions in the compartments were calculated from the total number of equivalents generated and the total number of equivalents of chloride in these compartments, obtained by Mohr titration as previously described [141].

In the lanthanum-zinc alloy experiments, the potential of the zinc pool against the lanthanum electrode and the temperature were measured as a function of time. Then the temperature was changed and another point taken. It appeared that no more than two points could be taken in a given experiment. This was true even for evacuated apparatus which, nevertheless, behaved better than that held under a positive pressure of purified argon. However, similar difficulties have been encountered previously, and might be ascribed to apparatus corrosion tending to remove the lanthanum

from the alloy [90], and/or to a poor contact with the tungsten lead caused by surface oxide formation.

All calculations were carried out on the University of Alberta I.B.M. 360 computer. The programs used are given in the appendix. Error limits given are the 95% confidence limits, with the hypothesis of a normal distribution of the errors.

III- R E S U L T S A N D D I S C U S S I O N

III-1. Standard potential of La(III)/La(0)

After elimination of questionable points, usually at lower concentrations range, 36 data points obtained in six different experiments (numbered runs 1 to 6 in appendix) were used. Potentials were measured as a function of La(III) concentration at a constant temperature. The time necessary to reach equilibrium varied from 5 to 30 minutes, the potential at equilibrium being constant with random variations of less than 2 mV/15 minutes, due to temperature fluctuations. Potentials at equilibrium were averaged over these small variations. Temperatures at equilibrium were also averaged for small fluctuations, usually of the order of 1°C. For all experiments the mean e.m.f. values were corrected to correspond to a standard electrode of unit mole fraction Pt(II) (S.M.F.P.E.) as a reference using the mean temperatures for each e.m.f.-concentration point; the platinum electrode is known to obey the Nernst equation with a two-electron process [141]. Plots of these e.m.f. values against the logarithm of the mole fraction of La(III) in the lanthanum compartment were linear (Fig. 8) showing that the lanthanum electrode is Nernstian in this solvent. For each run, the slope and the intercept of the straight lines representing
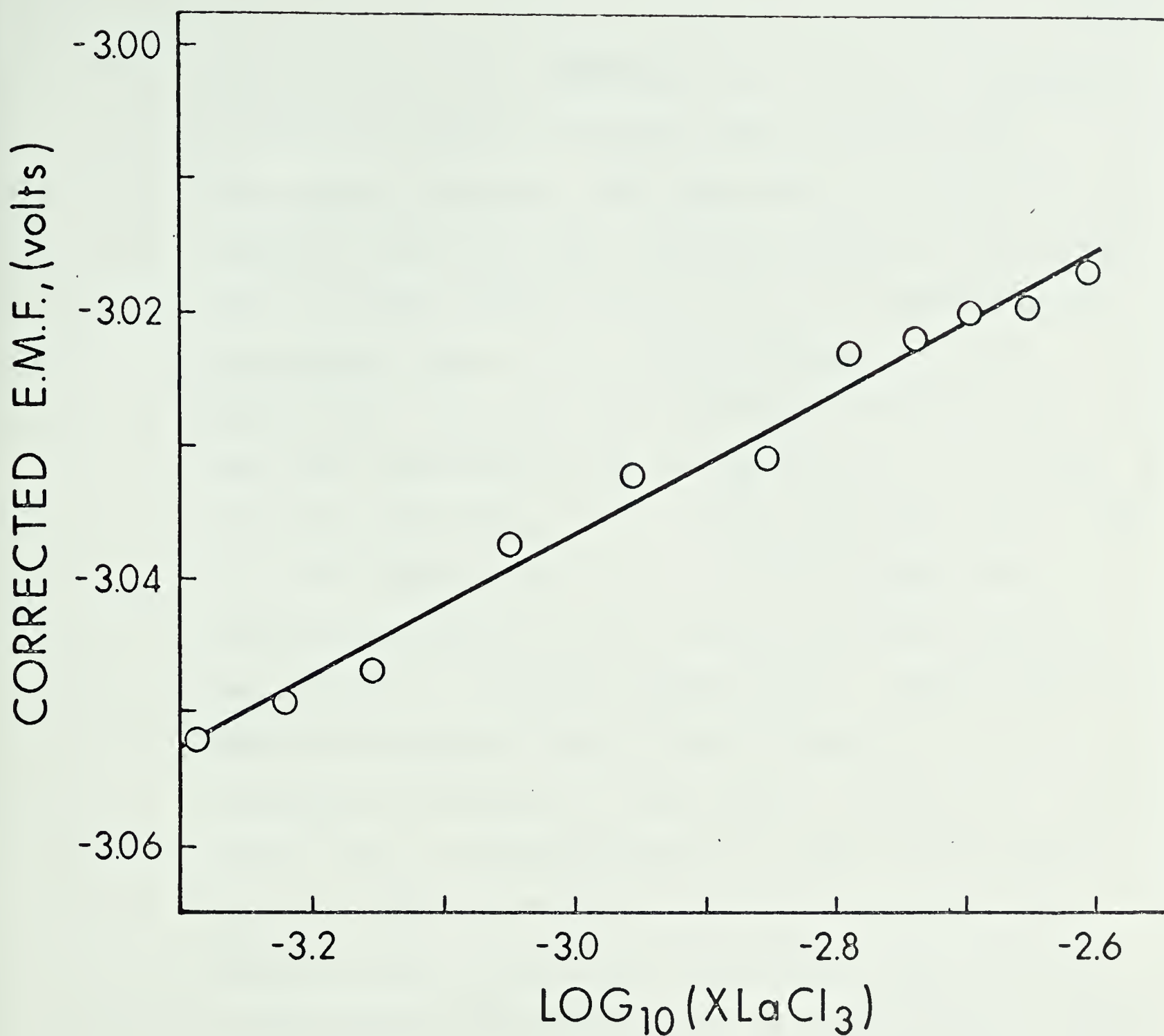
Figure 8.   Nernstian plot for the potential of the
La(III)/La(O) couple in LiCl-KCl eutectic,
corrected to S.M.F.P.E., for a typical
experiment (run no. 3, 447.4°C).

the variation of the corrected e.m.f. with the logarithm

of the mole fraction of La(III) were calculated by

least square analysis. The mean number of electrons

involved in the lanthanum electrode process as calculated

from the Nernst slopes was 3.0 ± 0.7, in agreement with

the expected value of 3. One experiment gave only a

single point, for which the intercept was calculated

using the theoretical slope of the line for a trivalent

lanthanum electrode process. These intercepts give a set

of values (Table 2 and Fig. 9) of the standard mole

fraction potentials of the lanthanum electrode against

the S.M.F.P.E. at various temperatures. Linear inter-

polation (fitting by least square analysis the best

straight line through the experimental temperature - e.m.f.

points) gave a standard potential of the La(III)/La(0)

couple at 450°C of -2.883 ± 0.007 volts, on the mole

fraction scale. The values obtained for this potential

on the molarity and molality scales at 450°C were -2.848

and -2.853 volts, respectively, with the same precision.

The temperature coefficient obtained was 4.4×10^{-4}

volts/°C with a standard error of 2×10^{-4} volts/°C.

Using the data of Laitinen and Pankey [137] for the chlorine

electrode against Pt(II) and the data of Yang and Hudson [101]

for the lanthanum electrode against Cl_2/Cl^-, Plambeck [102]

calculated, at 450°C, a standard potential for a lanthanum

TABLE 2

Standard potential of the La(III)/La(O) couple

against S.M.F.P.E. as a function of temperature

Mean temp. (°C)	Standard potential (V)
430.5	-2.886
446.3	-2.883
447.4	-2.877
450.5	-2.895
478.6	-2.873
545.2	-2.839
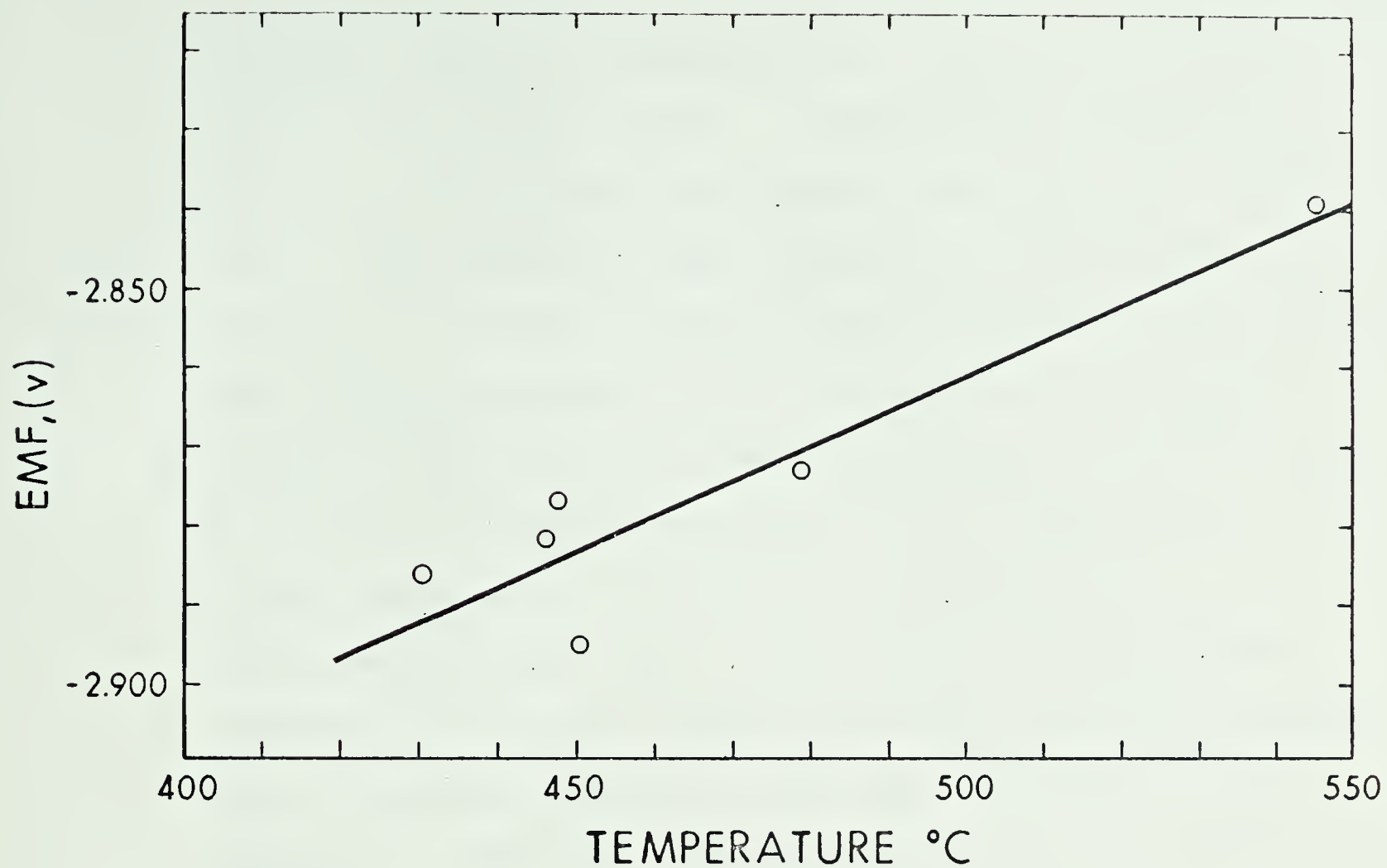
Figure 9.   Standard potential of the La(III)/La(O)

couple in LiCl-KCl eutectic, against

S.M.F.P.E., as a function of temperature.

electrode against Pt(II)/Pt(0) of -2.912 ± 0.005 volts,

on the mole fraction scale. A temperature coefficient

of 6.4×10^{-4} volts/°C can also be calculated from these

data. The potential value obtained from the present

study is 29 mV more positive than the previous value [102].

The problems involved in the calculation of potential

values at 450°C from the data of Yang and Hudson [101]

have been discussed by Plambeck [102,139]; these are

higher temperatures (480-550°C), concentrations

sufficiently higher than in the present work and other

studies [95,139], that Henrian behaviour cannot be assumed,

and a different reference electrode. Plambeck [102] also

points out that only a few experimental points are given

for each couple (ten for La(III)/La(0)). In a study of

the very similar Y(III)/Y(0) couple, Hoshino and Plambeck[95]

also find electrode potentials about 30 mV higher than

those calculated from the data of Yang and Hudson.

In this work, the temperature coefficient is not

known accurately. It agrees satisfactorily with the

value calculated from previous experiments in that this

value falls in the range of the rather large experimental

error.

III-2.   Liquid La-Zn alloy

The equation given by Johnson and Dillon [91] for

the solubility of lanthanum in liquid zinc (in g/kg):

$\log w = 9.573 - 8718/T$ gives a very low solubility

of lanthanum in zinc in the range 430-600°C (2.0×10^{-2} g/kg
at 500°C). It was not possible to prepare unsaturated
solutions for study due to the extremely small quantities
of lanthanum required for saturation. Attempts to prepare
the saturated solutions by electrodeposition of lanthanum
or by using a quantity of lanthanum slightly in excess
of the reported saturation level failed; higher (from
0.95 to 1.20 volts) and less stable (within 10 mV or more)
cell potentials than those reported below were observed,
possibly corresponding to unsaturated solutions. It was
found necessary to take a large excess of lanthanum
(1 to 5% by weight) to obtain the saturated solution.
The results discussed here are independent of further
addition of lanthanum (by electrodeposition on the zinc
pool). This shows that saturation had been reached, with
the excess lanthanum forming an intermetallic compound,
assumed here to be $LaZn_{11}$. Therefore at each temperature
point, the e.m.f. obtained was that of the cell:

(-)La(s)/LiCl-KCl(eutectic)-$LaCl_3$/La-Zn(saturated)(+).
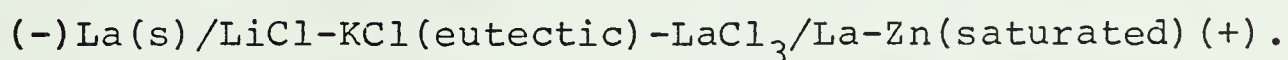
A time varying from one to six hours was found necessary
to reach equilibrium, the potential at equilibrium being
constant with variations of less than 0.5 mV/30 min in
most cases. Potentials at equilibrium were averaged for
these small variations. Temperatures were constant within
1°C as in the La(III)/La(0) potential experiments and
were similarly averaged. Thus a set of mean temperature-
e.m.f. values was obtained (Table 3). The best straight

TABLE 3

E.m.f. of the cell

(-)La/LiCl-KCl(eutectic)-LaCl$_3$/La-Zn(sat.)(+)

as a function of temperature

Mean temp. (°C)	Mean e.m.f. (V)
445.5	0.8584
450.4	0.8474
477.8	0.8368
495.5	0.8052
503.9	0.8014
511.1	0.8103
523.1	0.7947
585.5	0.7479
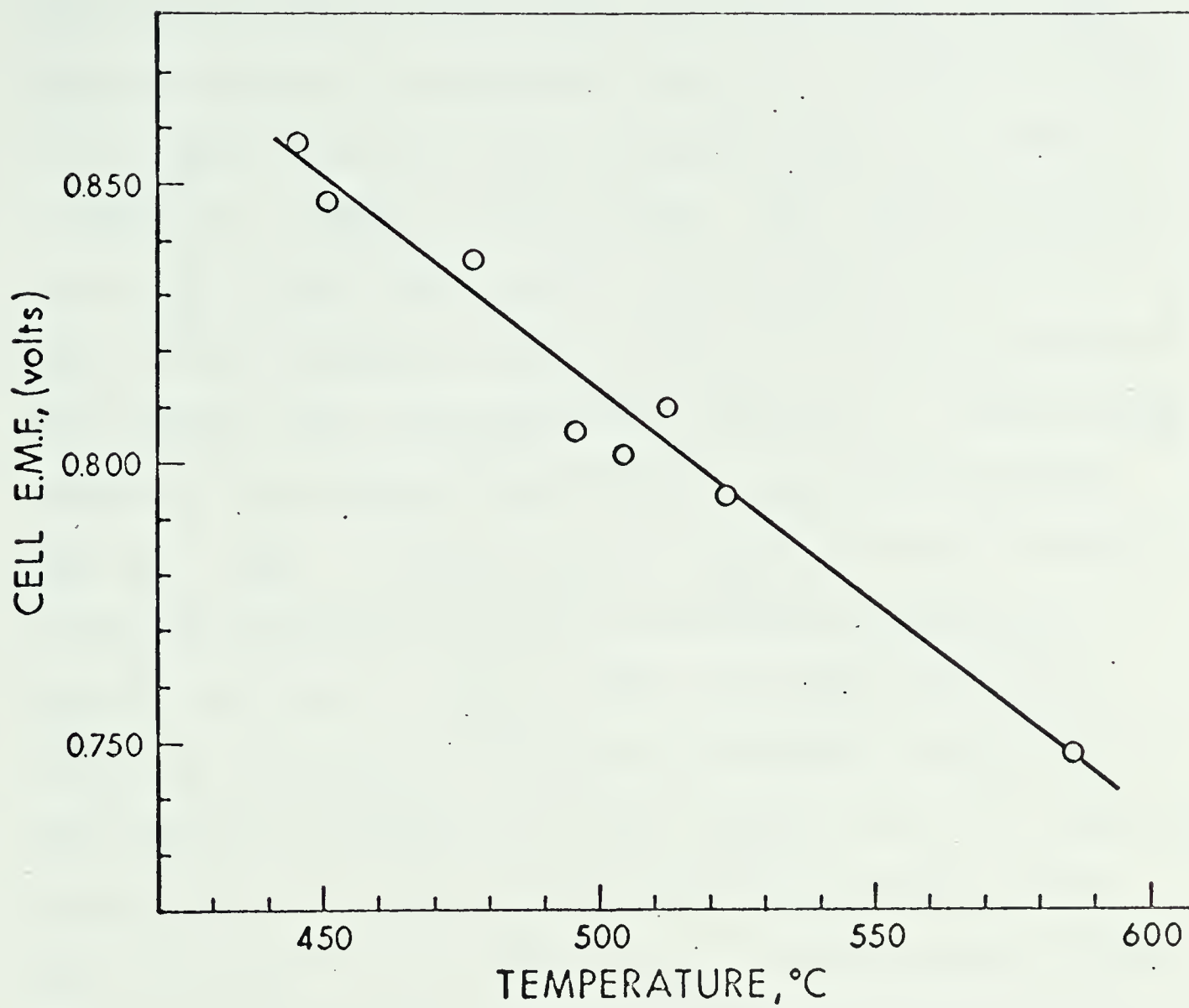
Figure 10. E.m.f. of the cell (-)La/LiCl-KCl(eut-ectic)-LaCl$_3$)/La-Zn(sat.) as a function of temperature.

line through these points (Fig. 10) was fitted by least

square analysis, its equation being: $E = 1.4085 - 7.71 \times 10^{-4}T$; this is valid in the range 430-600°C and gives,

at 450°C, $E = 0.8506 \pm 0.005$ volts. The overall process

occurring in the cell amounts to the formation of the

pure (solid) compound $LaZn_{11}$ from pure (solid) lanthanum

and (liquid) zinc saturated with lanthanum. If ΔG is the

change in free energy involved, it can be easily seen

that $\Delta G = g_{La}^m + 11(\mu_{Zn}(LaZn_{11}) - \mu_{Zn}(l))$; since, in the

liquid-solid phase equilibrium involved: $\mu_{Zn}(LaZn_{11}) = \mu_{Zn}(l)$, one has $\Delta G = g_{La}^m = -nFE$. Let ΔG_f°, $LaZn_{11}(s)$

be the free energy of formation of (solid) $LaZn_{11}$ from

pure (solid) lanthanum and pure (liquid) zinc, and a_{Zn} the

activity of the zinc in the saturated solution, then

ΔG_f°, $LaZn_{11}(s) = \Delta G + 11RT \ln a_{Zn}$. If one assumes ideal

behaviour of the zinc, since the solution of lanthanum is

very dilute, $a_{Zn} = 1 - x_{La}$, where x_{La} is the mole fraction

of lanthanum. Then, since x_{La} is very small, ΔG_f°, $LaZn_{11}(s) =$

$\Delta G - 11RT\ x_{La}$. At 500°C, the term $- 11RT\ x_{La}$ is -0.177

cal/mole, which is negligible. Thus ΔG_f°, $LaZn_{11}(s) =$

ΔG, so that ΔG_f°, $LaZn_{11}(s)$ is simply $-nFE$, where n=3.

In the same manner, the entropy of formation ΔS_f°,

$LaZn_{11}(s)$ is $nF(dE/dT)$ and the enthalpy formation ΔH_f°,

$LaZn_{11}(s)$ can be calculated by extrapolating the free

energy to 0°K. At 450°C for ΔG_f^o, $LaZn_{11}(s)$ and over
the temperature range 430-600°C for the other quantities,

$$\Delta G_f^o, LaZn_{11}(s) = -58.8 \pm 0.6 \text{ kcal/mole}$$
$$\Delta S_f^o, LaZn_{11}(s) = -53.4 \pm 8.0 \text{ cal/deg. mole}$$
$$\Delta H_f^o, LaZn_{11}(s) = -97.4 \pm 6.0 \text{ kcal/mole .}$$

In addition, ΔG_f^o, $LaZn_{11}(s)$ was calculated at temperatures
ranging from 430 to 600°C (Table 4), from the equation
ΔG_f^o, $LaZn_{11}(s) = -97.415 + 5.335 \times 10^{-2}T$, where T is in °K.
It appears that these e.m.f. values differ from those
obtained in a similar experiment by Johnson [134] by at
most 2%. The discrepancies are somewhat greater for the
entropy and enthalpy.

TABLE 4

Calculated free energy of formation of $LaZn_{11}$

as a function of temperature

Temp. (°C)	ΔG_f°, $LaZn_{11}$ (Kcal/mole).
430	-59.9
450	-58.8
500	-56.2
550	-53.5
600	-50.8

IV - C O N C L U S I O N

The thermodynamic theories examined in the intro-
duction provide a satisfactory basis for experimental
studies of alloys by e.m.f. methods. It should be noted,
however, that, especially in multicomponent systems,
their application requires a fair amount of work, in
both experiment and computations from experimental data,
but the results thus obtained are rigorous. The use
of a solution model reduces this work substantially, but
the results obtained are only a rough approximation,
especially at high concentrations.

From the experimental part of this work, a value for
the standard potential of the La(III)/La(0) couple at
450°C was calculated; the thermodynamic data computed
for the compound in equilibrium with the liquid saturated
lanthanum-zinc solution should be a useful contribution
to the knowledge of the properties of the lanthanum-zinc
system, which is still only partial.

Regarding possible practical applications in spent
nuclear fuel processing, it should be noticed that the
compound $LaZn_{11}$ appears from this study to be of much
greater stability than $UZn_{8.5}$; the standard energies of
formation at 450°C being -58.8 and -26.1 kcal/mole [48]
respectively. The standard potentials of pure uranium
and pure lanthanum (any scale since both metals are tri-
valent) in the LiCl-KCl eutectic melt differ by 0.630 V,

making electrochemical separation of these metals appear quite feasible. Using the free energies given above, the difference in standard potentials of uranium (saturated solution in zinc) and lanthanum (saturated solution in zinc), in the LiCl-KCl eutectic melt, is only 0.156 V at 450°C. The alloying with excess zinc thus appears unfavourable, since it reduces the feasibility of separating these elements electrochemically by a significant factor.

Since most rare earth metals are fission impurities[92,93], it might be desirable to study other rare earth-zinc systems as has been done here for the lanthanum-zinc system. Rare earth metals having very similar properties, it is likely that the same conclusion as here would be reached. This is confirmed by already existing data for the yttrium-zinc system [94,95], and on the Y(III)/Y(0) electrode potential in the LiCl-KCl eutectic [95,101,102], and for the cerium-zinc and erbium-zinc systems [96].

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VI - A P P E N D I X

Here follow the IBM 360 FORTRAN IV programs used in calculations from experimental data, according to the output given by the University of Alberta IBM 360 computer.

VI-1 . 'NERNST' program used in interpretation of results of La(III)/La(O)

experiments (mainline only)

```
C
C    MAINLINE FOR CALCULATION OF STANDARD POTENTIALS FROM NERNST EQUATION.
C
C    PURPOSE.
C
C    THIS PROGRAM CALCULATES THE STANDARD POTENTIAL OF THE METALLIC
C    ELECTRODE M IN THE CELL:
C
C                             R/R-ION//M-ION/M.
C
C    WHERE R IS A REFERENCE METALLIC ELECTRODE. IN THE MOLE FRACTION SCALE.
C    MEASUREMENTS ARE MADE AT CONSTANT TEMPERATURE, CONSTANT CONCENTRATION
C    IN R-ION AND VARIABLE CONCENTRATION IN M-ION. EXPERIMENTAL VALUES ARE
C    CORRECTED TO A MOLE FRACTION IN R-ION OF 1. BY MEANS OF NERNST EQUATION.
C    THE BEST STRAIGHT LINE REPRESENTING THE VARIATION OF THE CORRECTED EMF
C    AGAINST THE LOG OF THE MOLE FRACTION OF M-ION IS ESTABLISHED BY LEAST
C    SQUARE ANALYSIS, FOR EACH CONSTANT-TEMPERATURE EXPERIMENT. ITS SLOPE GIVES
C    THE NUMBER OF ELECTRONS INVOLVED IN THE M-ELECTRODE PROCESS, AND ITS
C    INTERCEPT THE STANDARD EMF AT THE EXPERIMENTAL TEMPERATURE, WHICH HAS
C    BEEN AVERAGED FOR SMALL FLUCTUATIONS. THE CASE WHEN THERE IS ONLY ONE
C    TEMPERATURE-EMF POINT IN ONE EXPERIMENT IS EXAMINED SEPARATELY.
C    THE BEST STRAIGHT LINE REPRESENTING THE TEMPERATURE DEPENDENCE OF THE
C    STANDARD POTENTIAL IS ESTABLISHED BY LEAST-SQUARE ANALYSIS. INTERCEPTS
C    ARE CALCULATED FOR SEVERAL TEMPERATURE ORIGINS. THE TEMPERATURE COEFFI-
C    -CIENT IS ALSO GIVEN. THE AVERAGE NUMBER OF ELECTRONS INVOLVED IN THE
C    M-ELECTRODE PROCESS IS CALCULATED. STANDARD DEVIATIONS ARE CALCULATED
C    ON ALL THESE QUANTITIES.
C    SEVERAL SUCH PROBLEMS CAN BE TREATED.
C
```

```
C  INPUT.
C
C  N,P ON ONE CARD FORMAT 2I6.
C  N: NUMBER OF CONSTANT TEMPERATURE EXPERIMENTS.
C  P: NUMBER OF ORIGINS FOR TEMPERATURES.
C
C  EKR,EKM,FACT,PTC,REC ON ONE CARD FORMAT 5D12.6.
C  EKR: NUMBER OF ELECTRONS INVOLVED IN REFERENCE ELECTRODE PROCESS.
C  EKM: NUMBER OF ELECTRONS INVOLVED IN WORKING ELECTRODE PROCESS.
C  FACT: FACTOR BY WHICH THE INDICATION OF THE COULOMETRIC CURRENT SOURCE
C        USED FOR GENERATING THE ELECTRODES HAS TO BE MULTIPLIED TO OBTAIN
C        MICROEQUIVALENTS.
C  PTC: EXPERIMENTAL ERROR ON TEMPERATURES.
C  REC: EXPERIMENTAL ERROR ON POTENTIALS.
C
C  TITLE ON ONE CARD FORMAT 19A4.
C
C  FOR EACH CONSTANT TEMPERATURE EXPERIMENT:
C
C  M,COULR,DR,DM, ON ONE CARD FORMAT I6,3D12.6.
C  M: NUMBER OF M-ION CONCENTRATION-TEMPERATURE POINTS.
C  COULR: INDICATION OF COULOMETRIC CURRENT SOURCE FOR REFERENCE ELECTRODE.
C  DR: NUMBER OF MOLES IN REFERENCE COMPARTMENT.
C  DM: NUMBER OF MOLES IN WORKING ELECTRODE COMPARTMENT.
C
C  M VALUES OF TEMPERATURE PUT IN ARRAY TC,ON M CARDS FORMAT D16.6.


C  M VALUES OF COULM AND EMF ON M CARDS FORMAT 2D16.6.
C  COULM: INDICATION OF COULOMETRIC CURRENT SOURCE FOR WORKING ELECTRODE.
C  P VALUES OF ORIGINS FOR TEMPERATURES PUT IN ARRAY TO,ON P CARDS FORMAT D16.6.
```

```
C     OUTPUT.
C
C     TITLE.
C
C     FOR EACH CONSTANT-TEMPERATURE EXPERIMENT:
C     NUMBER OF RUN.
C     TABLE OF M VALUES OF TEMPERATURE,MOLE FRACTION OF M-ION,LOG MOLE FRACTION OF
C     M-ION,CORRECTED EMF.
C     AVERAGE TEMPERATURE.
C     STANDARD DEVIATION ON AVERAGE TEMPERATURE.
C     STANDARD EMF AT AVERAGE TEMPERATURE.
C     SLOPE OF NERNSTIAN LINE.
C     THEORETICAL SLOPE OF NERNSTIAN LINE.
C     STANDARD DEVIATION ON SLOPE OF NERNSTIAN LINE.
C     NUMBER OF ELECTRONS INVOLVED IN M-ELECTRODE PROCESS.
C
C     FOR EACH ORIGIN OF TEMPERATURES:
C     ORIGIN OF TEMPERATURES IN DEGREES C.
C     STANDARD EMF AT THIS TEMPERATURE.
C     STANDARD DEVIATION ON THIS EMF.
C     TEMPERATURE COEFFICIENT OF STANDARD EMF.
C     STANDARD DEVIATION ON THIS COEFFICIENT.
C     AVERAGE NUMBER OF ELECTRONS INVOLVED IN M-ELECTRODE PROCESS.
C     STANDARD DEVIATION ON THIS NUMBER.
C
C
```

```
ISN 0002        IMPLICIT REAL*8(A-H,O-Z)
ISN 0003        REAL*8 T(20),TC(20),EMEC(20),YM(20),EMEO(20),EKME(20),TO(5),BS(5),
               1PRS(5),EKMES(20)
ISN 0004        REAL TITLE(19)
ISN 0005        INTEGER P

          C   R=(PERFECT GAS CONSTANT)/(FARADAY CONSTANT).R IN JOULES/DEGREES K.FARADAY
          C   CONSTANT IN COULOMBS.POTENTIALS IN VOLTS,TEMPERATURES IN DEGREES C OR K.
          C   MASSES IN MOLES AND CONCENTRATIONS IN MOLE FRACTIONS.
          C
ISN 0006        DATA R/ 0.198478197220D-2/
          C
          C   PRELIMINARY READING OF DATA.
          C
ISN 0007      1 READ(5,100,END=10) N,P,EKR,EKM,FACT,RTC,REC,TITLE
ISN 0008        WRITE(6,101) TITLE
ISN 0009        NI=0
          C
          C   LOOP READS AND PROCESSES DATA FOR EACH OF THE N CONSTANT-TEMPERATURE
          C   EXPERIMENTS.
          C
ISN 0010        DO 4 I=1,N
ISN 0011        READ(5,102) M,COULR,DR,DM

ISN 0012        COULR=COULR*FACT
ISN 0013        XR=COULR*1.0D-6/(EKR*DR)
```

```
ISN 0014        YR=DLOG10(XR)
ISN 0015        WRITE(6,103) I
ISN 0016        DO 2 J=1,M
ISN 0017      2 READ(5,104) TC(J)
ISN 0018        CALL AVERT(M,TC,TS,RT,RTC)
ISN 0019        T(1)=TS
ISN 0020        DO 3 J=1,M
ISN 0021        READ(5,105) COULM,EMF
ISN 0022        COULM=COULM*FACT
ISN 0023        XM=COULM*1.0D-6/(EKM*DM)
ISN 0024        YM(J)=DLOG10(XM)
ISN 0025        EMFC(J)=EMF+R*(TC(J)+0.27316D3)*YR/EKR
ISN 0026      3 WRITE(6,106) TC(J),XM,YM(J),EMFC(J)
ISN 0027        SLT=R*(T(1)+0.27316D3)/EKM

              C
              C IF M=1 CALCULATION IS NOT APPLICABLE;SUCH A RUN IS ELIMINATED FROM CAL-
              C -CULATION OF AVERAGE NUMBER OF ELECTRONS.
              C

ISN 0028        IF(M.EQ.1) GO TO 9
ISN 0029        CALL LEAST(M,YM,EMFC,0.0D0,SL,EMFS,RSL,RF)
ISN 0030        EMFO(I)=EMFS
ISN 0031        EKMF(I)=SLT*EKM/SL
ISN 0032        N1=N1+1
ISN 0033        EKMFS(N1)=EKMF(I)
ISN 0034      4 WRITE(6,107) T(I),RT,EMFO(I),SL,SLT,RSL,RF,EKMF(I)
ISN 0035        WRITE(6,108)
ISN 0036
```

```
C     LOOP CALCULATES BEST EMF-TEMPERATURE LINE FOR EACH TEMPERATURE ORIGIN.
C
C
ISN 0037          DO 7 I=1,P
ISN 0038          READ(5,109) TO(I)
ISN 0039          IF(I.GT.1) GO TO 5
ISN 0041          CALL LEAST(N,T,EMFO,TO(I),A,B,RA,RB)
ISN 0042          GO TO 6
ISN 0043        5 CALL LEAST(M,T,EMFO,TO(I),B,RB)
ISN 0044        6 BS(I)=B
ISN 0045        7 RBS(I)=RB
ISN 0046          DO 8 I=1,P
ISN 0047        8 WRITE(6,110) TO(I),BS(I),RBS(I)
ISN 0048          WRITE(6,111) A,RA
C
C     AVERAGE NUMBER OF ELECTRONS AND STANDARD DEVIATION ON IT ARE CALCULATED.
C
ISN 0049          CALL AVERT(N1,EKNE,EKMS,RKM,0.000)
ISN 0050          WRITE(6,112) EKMS,RKM
C
C     CONTROL IS TRANSFERRED TO STATEMENT 1 FOR ANOTHER PROBLEM TO BE TREATED.
C
ISN 0051          GO TO 1
C
C     IN CASE M=1 STANDARD EMF IS CALCULATED USING THEORETICAL SLOPE OF
C     NERNSTIAN LINE.STANDARD DEVIATION IS TAKEN AS EXPERIMENTAL ERROR AND
C     NUMBER OF ELECTRONS AS ASSUMED THEORETICAL ONE (EKM).
C
ISN 0052        9 EMFO(I)=EMFC(I)-B*(T(I)+0.27316D2)*VM(I)/EKM
```

```
ISN 0053        T(I)=TC(I)
ISN 0054        SL=SLT
ISN 0055        RE=REC
ISN 0056        DT=DTC
ISN 0057        EKMF(I)=EKM
ISN 0058        GO TO 4
ISN 0059     10 STOP
ISN 0060    100 FORMAT(2I6/5D12.6/19A4)
ISN 0061    101 FORMAT(1H1,19A4//1H )
ISN 0062    102 FORMAT(I6,3D12.6)
ISN 0063    103 FORMAT(1H // '   RUN NO ',I4// '  TEMPERATURE      MOLE FRACTION
               1       LOG MOLE FR.    CORRECTED EMF '/1H )
ISN 0064    104 FORMAT(D16.6)
ISN 0065    105 FORMAT(2D16.6)
ISN 0066    106 FORMAT(2D16.6,D20.6,D16.6)
ISN 0067    107 FORMAT(1H // ' TEMPERATURE= ',D16.6/' STANDARD DEVIATION ON TEMPERAT
               1URE= ',D16.6/' STANDARD EMF= ',D16.6/' SLOPE= ',D16.6/' THEORETICAL
               2 SLOPE= ',D16.6/' STANDARD DEVIATION ON EMF= ',D16.6/' STANDARD DE
               3VIATION ON SLOPE= ',D16.6/' NUMBER OF ELECTRONS INVOLVED= ',D12.4)
ISN 0068    108 FORMAT(1H ///)
ISN 0069    109 FORMAT(D16.6)
ISN 0070    110 FORMAT(1H // ' TO= ',D16.6/ ' STANDARD EMF AT TO= ',D16.6/ ' STAND
               1ARD DEVIATION ON EMF AT TO= ',D16.6)
ISN 0071    111 FORMAT(1H // ' TEMPERATURE COEFFICIENT OF STANDARD EMF= ',D16.6/
               1 STANDARD DEVIATION ON IT= ',D16.6)
ISN 0072    112 FORMAT(1H // ' AVERAGE NUMBER OF ELECTRONS INVOLVED= ',D12.4/ ' ST
               1ANDARD DEVIATION ON IT= ',D12.4)
ISN 0073        END

****** END OF COMPILATION ******
```

VI-2. 'ZINC' program used in interpretation of results of

lanthanum-zinc alloy experiments (mainline only)

```
C.........................................................................
C    MAINLINE FOR THERMODYNAMIC CALCULATIONS FROM EMF DATA.
C
C    PURPOSE.
C
C    THIS PROGRAM CALCULATES THERMODYNAMIC DATA FOR AN INTERMETALLIC
C    COMPOUND OF TWO METALS M1 AND M2 FROM THE EMF OF THE CELL:
C
C    M2/SOLUTION OF M2 ICN /SATURATED SOLUTION OF M2 IN M1
C
C    IT FIRST ESTABLISHES THE TEMPERATURE DEPENDENCE OF THIS EMF ON A LINEAR
C    BASIS; INTERCEPT IS CALCULATED FOR SEVERAL REFERENCE TEMPERATURES TAKEN
C    AS ORIGINS, THEN IT CALCULATES THE FREE ENERGY AT SEVERAL REFERENCE TEMPE-
C    -RATURES AND THE ENTROPY AND ENTHALPY, FOR THE FORMATION OF THE COMPOUND
C    IN EQUILIBRIUM WITH THE M1-M2 SOLUTION, AND FINALLY THE FREE ENERGY AS A
C    FUNCTION OF TEMPERATURE. STANDARD DEVIATIONS ARE CALCULATED ON ALL THESE
C    QUANTITIES.
C    SEVERAL SUCH PROBLEMS CAN BE TREATED.
C
C    INPUT.
C
C    N,P,Q ON ONE CARD FORMAT 3I6.
C    N:   NUMBER OF TEMPERATURE-EMF POINTS.
C    P:   NUMBER OF REFERENCE TEMPERATURES.
C    Q:   NUMBER OF FREE ENERGIES TO BE CALCULATED AS A FUNCTION OF TEMPE-
C         -RATURE.
```

```
C     EK,TA,PAS,RTC,REC ON ONE CARD FORMAT 5D16.6.
C     EK:  NUMBER OF ELECTRONS INVOLVED.
C     TA:  INITIAL TEMPERATURE FOR FREE ENERGY CALCULATIONS.
C     PAS: TEMPERATURE INTERVAL FOR FREE ENERGY CALCULATIONS.
C     RTC: EXPERIMENTAL ERROR ON TEMPERATURE.
C     REC: EXPERIMENTAL ERROR ON POTENTIALS.
C
C     TITLE ON ONE CARD FORMAT 19A4.
C
C     FOR EACH OF THE N DATA POINTS:
C     M:  NUMBER OF TEMPERATURE AND EMF VALUES TO BE PROCESSED TO OBTAIN A
C         COUPLE OF AVERAGE VALUES FOR ONE POINT, ON ONE CARD FORMAT I6.
C     M TEMPERATURE-EMF COUPLES OF VALUES PUT IN ARRAYS TC AND EC ON M CARDS
C         FORMAT 2D16.6.
C
C     TO:  ARRAY WHERE P REFERENCE TEMPERATURES ARE PUT, ON P CARDS FORMAT D16.6.
C
C
C     OUTPUT.
C
C     TITLE, EK.
C
C     TABLE OF AVERAGE TEMPERATURES AND EMFS FOR THE N DATA POINTS, WITH STAN-
C     -DARD DEVIATIONS.
C
C     VALUES OF INTERCEPTS AT DIFFERENT TO'S AND SLOPE OF TEMPERATURE-EMF
C     STRAIGHT LINE, WITH STANDARD DEVIATIONS ON ALL THESE QUANTITIES.
```

```
C     VALUES OF FREE ENERGY AT DIFFERENT TO'S, ENTROPY, ENTHALPY, WITH STANDARD
C     DEVIATIONS ON ALL THESE QUANTITIES.
C
C     TABLE OF Q VALUES OF FREE ENERGY, FROM TA TO TA + Q TIMES PAS.
C
C
ISN 0002       IMPLICIT REAL*8(A-H,O-Z)
ISN 0003       INTEGER P,Q
ISN 0004       REAL*8 TC(10),FC(10),T(10),E(10),RT(10),RE(10),TO(5),GO(5),RG(5)
ISN 0005       REAL TITLE(10)
C
C     CON:  CONVERSION FACTOR FROM EMFS TO FREE ENERGIES, EMFS IN VOLTS, ALL
C     THERMODYNAMIC QUANTITIES IN CALORIES AND DEGREES C.
C
ISN 0006       DATA CON/0.23054'15308405/
C
C     PRELIMINARY READING OF DATA.
C
ISN 0007     1 READ(5,100,END=9) N,P,Q,FK,TA,PAS,RTC,REC,TITLE
ISN 0008       WRITE(6,101) TITLE,FK
ISN 0009       WRITE(6,102)
C
C     LOOP READS TEMPERATURE-EMF DATA FOR N SETS OF M VALUES, AVERAGES THESE,
C     AND WRITES M COUPLES OF AVERAGE VALUES WITH STANDARD DEVIATIONS.
C
ISN 0010       DO 3 I=1,N
```

```
ISN 0011        READ(5,102) M
ISN 0012        DO 2 J=1,M
ISN 0013      2 READ(5,104) TC(J),EC(J)
ISN 0014        CALL AVERT(M,TC,TS,RTS,RTC)
ISN 0015        T(I)=TS
ISN 0016        RT(I)=RTS
ISN 0017        CALL AVERT(M,EC,ES,RES,REC)
ISN 0018        E(I)=ES
ISN 0019        RE(I)=RES
ISN 0020      3 WRITE(6,105) T(I),RT(I),E(I),RE(I)

      C LINEAR TEMPERATURE DEPENDENCE OF EMFS IS ESTABLISHED BY LEAST-SQUARE
      C ANALYSIS. INTERCEPTS ARE CALCULATED FOR SEVERAL ORIGINS. RESULTS ARE
      C WRITTEN.
      C FREE ENERGY IS CALCULATED AT SEVERAL REFERENCE TEMPERATURES AND IS
      C WRITTEN. ENTROPY AND ENTHALPY ARE CALCULATED AND WRITTEN. STANDARD DEVIA-
      C -TIONS ARE CALCULATED AND WRITTEN.
      C

ISN 0021        WRITE(6,106)
ISN 0022        DO 6 I=1,P
ISN 0023        READ(5,107) TO(I)
ISN 0024        IF(I.GT.1) GO TO 4
ISN 0026        CALL LEAST(N,T,E,TO(I),A,R,RA,RR)
ISN 0027      4 CALL LEAST(N,T,E,TO(I),B,RB,RR)
ISN 0028        WRITE(6,108) TO(I),B,RB
ISN 0029        IF(TO(I).EQ.-0.2731603) GO TO 5
ISN 0030        GO(I)=-EK*CON*B
ISN 0031        RC(I)=EK*CON*RB
ISN 0033      5 IF(TO(I).NE.-0.2731603) GO TO 6
```

```
ISN  0035        H=-FK*CON*B
ISN  0036        RH=FK*CON*BB
ISN  0037      6 CONTINUE
ISN  0038        WRITE(6,109) A,BA
ISN  0039        S=FK*CON*A
ISN  0040        RS=FK*CON*BA
ISN  0041        WRITE(6,110)
ISN  0042        DO 7 J=1,P
ISN  0043        IF(TO(I).EQ.-0.27316D3) GO TO 7
ISN  0044        WRITE(6,111) TO(I),GO(I),RG(I)
ISN  0046      7 CONTINUE
ISN  0047        WRITE(6,112) S,RS,H,RH

C
C     LOOP CALCULATES AND WRITES FREE ENERGIES AS A FUNCTION OF TEMPERATURE.
C

ISN  0048        TP=0.0D0
ISN  0049        GA=H-(TA+0.27316D3)*S
ISN  0050        WRITE(6,113)
ISN  0051        DO 8 I=1,Q
ISN  0052        G=GA-TD*S
ISN  0053        WRITE(6,114) TA,G
ISN  0054        TA=TA+DAS
ISN  0055      8 TD=TD+DAS

C
C     CONTROL IS TRANSFERRED TO STATEMENT 1 FOR ANOTHER PROBLEM TO BE TREATED.
C
C
```

```
ISN 0056          GO TO 1
ISN 0057        9 STOP
ISN 0058      100 FORMAT(3I6/5D16.6/10A4)
ISN 0059      101 FORMAT(1H1,19A4/ ' NUMBER OF ELECTRONS INVOLVED= ',D16.6)
ISN 0060      102 FORMAT(1H ///  ' TEMPERATURE     S. D. ON TEMP.  MEASURED EMF
                 1 S. D. ON EMF ')
ISN 0061      103 FORMAT(I5)
ISN 0062      104 FORMAT(2D16.6)
ISN 0063      105 FORMAT(4D16.6)
ISN 0064      106 FORMAT(1H /// ' TEMPERATURE DEPENDENCE OF EMF ')
ISN 0065      107 FORMAT(D16.6)
ISN 0066      108 FORMAT(' TO= ',D16.6, ' EMF AT TO= ',D16.6/ ' STANDARD DEVIATION O
                 1N EMF= ',D16.6)
ISN 0067      109 FORMAT(' TEMPERATURE COEFF. OF EMF= ',D16.6/ ' STANDARD DEVIATION
                 1 ON TEMPERATURE COEFF.= ',D16.6)
ISN 0068      110 FORMAT(1H /// ' THERMODYNAMIC FUNCTIONS AT REFERENCE TEMPERATURES
                 1 ')
ISN 0069      111 FORMAT(' TO= ',D16.6, ' FREE ENERGY AT TO= ',D16.6/ ' STANDARD DE
                 1VIATION ON FREE ENERGY= ',D16.6)
ISN 0070      112 FORMAT(' ENTROPY= ',D16.6/ ' STANDARD DEVIATION ON ENTROPY= ',D16.6
                 1/ ' ENTHALPY= ',D16.6/ ' STANDARD DEVIATION ON ENTHALPY= ',D16.6)
ISN 0071      113 FORMAT(1H /// ' CALCULATION OF FREE ENERGIES AS A FUNCTION OF TEMP
                 1ERATURE ///  ' TEMPERATURE     FREE ENERGY ')
ISN 0072      114 FORMAT(2D16.6)
ISN 0073          END

******  END OF COMPILATION ******
```

VI-3. SUBROUTINE 'AVERT' (averaging of data)

```
C
C
C     SUBROUTINE AVERT.
C
C     PURPOSE.
C
C     SUBROUTINE AVERAGES M VALUES OF A QUANTITY PUT IN ARRAY TC, AND GIVES
C     STANDARD DEVIATION ON MEAN VALUE.
C
C     INPUT.
C
C     VALUE OF M.
C     M VALUES IN ARRAY TC.
C     EPS:  VALUE OF EXPERIMENTAL ERROR, TO REPLACE STANDARD DEVIATION IF THIS
C     IS FOUND TO BE 0.
C
C     OUTPUT.
C
C     MEAN VALUE TS.
C     STANDARD DEVIATION ON TS, ERT.
C
C
```

```
ISN 0002        SUBROUTINE AVDOT(M,TC,TS,EDT,ERS)
ISN 0003        IMPLICIT REAL*8(A-H,O-Z)
ISN 0004        REAL*8 TC(200)
C
C     LOOP CALCULATES SUM OF M VALUES OF TC.
C
ISN 0005        SIGMA=0.000
ISN 0006        DO 1 I=1,M
ISN 0007      1 SIGMA=SIGMA+TC(I)
C
C     MEAN VALUE IS CALCULATED.
C
ISN 0008        TS=SIGMA/DFLOAT(M)
C
C     IF M IS 1 CALCULATION NOT APPLICABLE AND EDT SET TO ERS.
C
ISN 0009        IF(M.LT.2) GO TO 3
C
C     LOOP CALCULATES SUM OF SQUARE DEVIATIONS.
C
ISN 0010        SIGMA=0.000
ISN 0011        DO 2 I=1,M
ISN 0012      2 SIGMA=SIGMA+(TC(I)-TS)**2
C
C     STANDARD DEVIATION IS CALCULATED.
C
ISN 0014        EDT=DSQRT(SIGMA/DFLOAT(M-1))
C
C     IF STANDARD DEVIATION FOUND TO BE 0.0 EDT IS GIVEN THE VALUE OF ERS.
C
ISN 0015        IF(EDT.EQ.0.0000) GO TO 3
ISN 0016        RETURN
ISN 0017      3 EDT=ERS
ISN 0018        RETURN
ISN 0020        END

****** END OF COMPILATION ******
```

VI-4. SUBROUTINE 'LEAST' (linear least squares)

```
C .........................................................
C
C     SUBROUTINE LEAST.
C
C     PURPOSE.
C     SUBROUTINE CALCULATES SLOPE AND INTERCEPT OF THE BEST STRAIGHT LINE
C     PASSING THROUGH N POINTS WHOSE ABSCISSAS ARE PUT IN ARRAY X AND ORDINATES
C     IN ARRAY Y BY LEAST SQUARE ANALYSIS. CALCULATION IS DONE WITH XO AS ORIGIN
C     FOR X'S. ENTRY LEAST1 ENABLES ONE TO DO ONLY CALCULATION OF SLOPE IF DE-
C     -SIRED.
C
C     INPUT.
C
C     N AND N COUPLES OF VALUES IN ARRAYS X AND Y.
C     XO:   ORIGIN FOR Y'S.
C
C     OUTPUT.
C
C     A:    SLOPE (NO OUTPUT IF ENTRY LEAST1).
C     B:    INTERCEPT WITH X=XO.
C     T:    STANDARD DEVIATION ON INTERCEPT WITH X=XO.
C
C     REMARK.
C
C     SUBROUTINE USE IS MEANINGLESS FOR N=1. MAINLINE SHOULD AVOID CALLING IT
C     IN THAT CASE.
C
C .........................................................
```

```fortran
ISN 0002          SUBROUTINE LEAST(N,X,Y,X0,A,B,S,T)
ISN 0003          IMPLICIT REAL*8(A-H,O-Z)
ISN 0004          REAL*8 X(20),X1(20),Y(20)
ISN 0005          INTEGER OPT
ISN 0006          OPT=0
ISN 0007          GO TO 1
ISN 0008          ENTRY LEAST1(N,X,Y,X0,B,T)
ISN 0009          OPT=1
ISN 0010        1 SX=0.0D0
ISN 0011          SXX=0.0D0
ISN 0012          SXY=0.0D0
ISN 0013          SY=0.0D0
C
C     LOOP CALCULATES SUMS OF X'S, SQUARE X'S, XY'S, AND OF Y'S.
C
ISN 0014          DO 2 I=1,N
ISN 0015          X1(I)=X(I)-X0
ISN 0016          SX=SX+X1(I)
ISN 0017          SXX=SXX+X1(I)*X1(I)
ISN 0018          SXY=SXY+X1(I)*Y(I)
ISN 0019        2 SY=SY+Y(I)
C
C     LINEAR EQUATIONS GIVING A AND B ARE SOLVED.
C
ISN 0020          DELTA=SXX*DFLOAT(N)-SX*SX
```

```
ISN 0021        IF(OPT.EQ.0) A=(SXY*DFLOAT(N)-SX*SY)/DELTA
ISN 0022        B=(SXX*SY-SXY*SX)/DELTA

C
C       IF N LESS THAN 3 CALCULATION OF STANDARD DEVIATIONS NOT APPLICABLE AND
C       THESE ARE SET TO 0.
C

ISN 0024        IF(N.LT.3) GO TO 4
ISN 0026        SIGMA=0.0D0
ISN 0027        DO 2 I=1,N
ISN 0028      2 SIGMA=SIGMA+(Y(I)-A*X1(I)-B)**2

C
C       CALCULATIONS OF S AND T.
C

ISN 0030        IF(OPT.EQ.0) S=DSQRT(SIGMA*DFLOAT(N)/(DELTA*DFLOAT(N-2)))
ISN 0031        T=DSQRT(SXX*SIGMA/(DELTA*DFLOAT(N-2)))
ISN 0032        GO TO 5
ISN 0033      4 IF(OPT.EQ.0) S=0.0D0
ISN 0035        T=0.0D0
ISN 0036      5 RETURN
ISN 0037        END

***** END OF COMPILATION ******
```

VI-5. Output of 'NERNST' Program

STANDARD POTENTIAL OF A LANTHANUM ELECTRODE IN LICL-KCL VS PLATINUM REF.

RUN NO 1

TEMPERATURE	MOLE FRACTION	LOG MOLE FR.	CORRECTED EMF
0.4305600 03	0.2845600-03	-0.2412850 01	-0.3042420 01
0.4305600 03	0.4415780-03	-0.3354090 01	-0.3034090 01
0.4303800 03	0.5519650-03	-0.3258000 01	-0.3032870 01
0.4305000 03	0.6623400-03	-0.3178000 01	-0.3026400 01
0.4305000 03	0.9851770-03	-0.3052070 01	-0.3023000 01
0.4305000 03	0.1102030-02	-0.2957060 01	-0.3020000 01

TEMPERATURE=   0.4305000 03
STANDARD DEVIATION ON TEMPERATURE=   0.6572670-01
STANDARD EMF=   -0.2985550 01
SLOPE=   0.4544500-01
THEORETICAL SLOPE=   0.4655370-01
STANDARD DEVIATION ON EMF=   0.3210530-02
STANDARD DEVIATION ON SLOPE=   0.1032340-01
NUMBER OF ELECTRONS INVOLVED=   0.30740 01

RUN NO   2

TEMPERATURE	MOLE FRACTION	LOG MOLE FR.	CORRECTED EMF
0.4465000D 03	0.1241173D-02	-0.2907253D 01	-0.3073647D 00
0.4459650D 03	0.1502010D-02	-0.2821448D 01	-0.3083777D 00
0.4471700D 03	0.1774420D-02	-0.2751855D 01	-0.3080611D 00
0.4458800D 03	0.1917800D-02	-0.2717566D 01	-0.3072285D 00
0.4460000D 03	0.2107840D-02	-0.2676766D 01	-0.3027728D 00
0.4462000D 03	0.2200620D-02	-0.2623836D 01	-0.3024234D 00

TEMPERATURE = 0.4462822E 03
STANDARD DEVIATION ON TEMPERATURE = 0.4886699D 00
STANDARD EMF = -0.2889700D 01
SLOPE = 0.5360410-01
THEORETICAL SLOPE = 0.4750790-01
STANDARD DEVIATION ON EMF = 0.6951738-02
STANDARD DEVIATION ON SLOPE = 0.1000060-01
NUMBER OF ELECTRONS INVOLVED = 0.2664D 01

RUN NO   4

TEMPERATURE	MOLE FRACTION	LOG MOLE FR.	CORRECTED EMF
0.4508000 03	0.4057850-03	-0.3392350 01	-0.3033540 01
0.4507500 03	0.4630320-03	-0.3343390 01	-0.3029540 01
0.4506000 03	0.5787850-03	-0.3237480 01	-0.3026000 01
0.4502600 03	0.4948150-03	-0.3158130 01	-0.3022890 01
0.4504000 03	0.6260070-03	-0.3033300 01	-0.3017440 01
0.4500000 03	0.1157490-02	-0.2936480 01	-0.3014810 01

TEMPERATURE=   0.4504680 03
STANDARD DEVIATION ON TEMPERATURE=   0.3070220 00
STANDARD EMF= -0.2805020 01
SLOPE=   0.4054530-01
THEORETICAL SLOPE=   0.4787480-01
STANDARD DEVIATION ON EMF=   0.1085040-02
STANDARD DEVIATION ON SLOPE=   0.6324420-02
NUMBER OF ELECTRONS INVOLVED=   0.35420 01

RUN NO   5

TEMPERATURE	MOLE FRACTION	LOG MOLE FR.	CORRECTED EMF
0.4787500 03	0.3570650-03	-0.3446160 01	-0.3052740 01
0.4786200 03	0.4007540-03	-0.3388010 01	-0.3048700 01
0.4783800 03	0.5117200-03	-0.3301200 01	-0.3043620 01
0.4787000 03	0.6135000-03	-0.3212120 01	-0.3030020 01
0.4785000 03	0.8181000-03	-0.3087150 01	-0.3032660 01
0.4787000 03	0.1022270-02	-0.2980240 01	-0.3028720 01

TEMPERATURE=   0.4785080 03
STANDARD DEVIATION ON TEMPERATURE=   0.1422450 00
STANDARD EMF= -0.2877800 01
SLOPE=   0.5170450-01
THEORETICAL SLOPE=   0.4073650-01
STANDARD DEVIATION ON EMF=   0.1480180-02
STANDARD DEVIATION ON SLOPE=   0.4024600-02
NUMBER OF ELECTRONS INVOLVED=   0.28860 01

RUN NO. 4

TEMPERATURE	MOLE FRACTION	LOG MOLE FR.	CORRECTED EMF
0.545250D 03	0.524062D-04	-0.407380D 01	-0.305024D 01

TEMPERATURE= 0.545250D 03
STANDARD DEVIATION ON TEMPERATURE= 0.100000D 00
STANDARD EMF= -0.288250D 01
SLOPE= 0.541455D-01
THEORETICAL SLOPE= 0.541455D-01
STANDARD DEVIATION ON EMF= 0.148018D-02
STANDARD DEVIATION ON SLOPE= 0.500000D-02
NUMBER OF ELECTRONS INVOLVED= 0.30000D 01

TO= 0.450000D 03
STANDARD EMF AT TO= -0.288261D 01
STANDARD DEVIATION ON EMF AT TO= 0.357748D-02

TO= 0.0
STANDARD EMF AT TO= -0.307860D 01
STANDARD DEVIATION ON EMF AT TO= 0.404225D-01

TO= -0.273160D 03
STANDARD EMF AT TO= -0.310757D 01
STANDARD DEVIATION ON EMF AT TO= 0.629684D-01

TEMPERATURE COEFFICIENT OF STANDARD EMF= 0.435544D-03
STANDARD DEVIATION ON IT= 0.863784D-04

AVERAGE NUMBER OF ELECTRONS INVOLVED= 0.29460D 01
STANDARD DEVIATION ON IT= 0.36210D 00

VI-6. Output of 'ZINC' program

THERMODYNAMICS OF A DILUTE SATURATED LA-ZN ALLOY FROM EMF DATA

NUMBER OF ELECTRONS INVOLVED= 0.200000D 01

TEMPERATURE	S.D. ON TEMP.	MEASURED EMF	S.D. ON EMF
0.445518D 03	0.7205420 00	0.8694640 00	0.2740460-03
0.4504000 03	0.1000000 00	0.8474000 00	0.7047460-03
0.4777620 03	0.1060660 00	0.8357750 00	0.1581140-03
0.4654640 03	0.2240340 00	0.8052000 00	0.2300480-03
0.5029750 03	0.1031200 01	0.8014370 00	0.1645440-02
0.5117320 03	0.1271150 01	0.8103230 00	0.5772500-02
0.5231000 03	0.1238700 00	0.7947000 00	0.1851640-02
0.5855420 03	0.1001020 00	0.7470080 00	0.1538970-02

TEMPERATURE DEPENDENCE OF EMF

T0= 0.4500000 03 EMF AT T0= 0.8506530 00
STANDARD DEVIATION ON EMF= 0.3867750-02
T0= 0.0 EMF AT T0= 0.1107780 01
STANDARD DEVIATION ON EMF= 0.3006360-01
T0= -0.2731600 03 EMF AT T0= 0.1408500 01
STANDARD DEVIATION ON EMF= 0.4642340-01
TEMPERATURE COEFF. OF EMF= -0.7713070-03
STANDARD DEVIATION ON TEMPERATURE COEFF.= 0.6002620-04

THERMODYNAMIC FUNCTIONS AT REFERENCE TEMPERATURES
T0= 0.4500000 03 FREE ENERGY AT T0= -0.5883320 05
STANDARD DEVIATION ON FREE ENERGY= 0.2675030 03
T0= 0.0 FREE ENERGY AT T0= -0.8294140 05
STANDARD DEVIATION ON FREE ENERGY= 0.2070270 04
ENTROPY= -0.5335160 02
STANDARD DEVIATION ON ENTROPY= 0.4151550 01
ENTHALPY= -0.8741490 05
STANDARD DEVIATION ON ENTHALPY= 0.3810750 04

CALCULATION OF FREE ENERGIES AS A FUNCTION OF TEMPERATURE

TEMPERATURE	FREE ENERGY